

## A., II.—Organic Chemistry

JANUARY, 1943.

## I.—ALIPHATIC.

**Preparation of derivatives of  $\psi$ -butylene.** V. S. Batalin and P. G. Ugniumov (*Sintet. Kautschuk*, 1936, No. 6, 8—16; cf. A., 1936, 62).—Direct chlorination of  $\psi$ -butylene at  $-10^\circ$  yields  $(\text{CHMeCl})_2$ .  $\text{Cl}\cdot[\text{CHMe}]_2\cdot\text{OH}$  and  $\text{NaOH}$  afford  $\psi$ -butylene oxide, whence  $(\text{CHMe}\cdot\text{OH})_2$ ,  $\text{COMeEt}$ , mono-, di-, and tri-butanolamines were obtained. CH. Abs. (c)

**Preparation of alkyl halides.**—See B., 1942, II, 355.

**Manufacture of methyl bromide.**—See B., 1942, II, 354.

**Preparation of ethyl chloride.**—See B., 1942, II, 354.

**Mechanism of additions to double bonds. XIV. Nature of the activated complex in bimolecular diene syntheses.**—See A., 1943, I, 19.

**Raman effect and problems of constitution. XVIII. Hexachlorobutadiene and octachlorocyclopentene.**—See A., 1942, I, 387.

**Production of additive products of acetylene and alcohols.**—See B., 1942, II, 357.

**Acidic and basic catalysis in urethane formation.**—See A., 1943, I, 20.

**Anhydrides of mannitol.** S. Müller (*Magyar Biol. Kutató Intézet Munkái*, 1935—6, 8, 405—413).—Mannitol dibenzoate tri-*p*-toluenesulphonate can be disproportionated into mannitol dibenzoate tetra-*p*-toluenesulphonate and anhydromannitol dibenzoate di-*p*-toluenesulphonate, which is stable to alkali. The varying stability of compounds of the group is explained by at. models. CH. Abs. (c)

**Stabilisation of ethers.**—See B., 1942, II, 357.

**Production of ethylene glycol monoethyl ether.**—See B., 1942, II, 353.

**Synthesis of dimethyl ethers of the two enantiomorphic  $\alpha$ -butyrins and their hydrolysis by lipases.** E. Baer and H. O. L. Fischer (*J. Biol. Chem.*, 1942, 145, 61—68).—Serum-lipase of rats and guinea-pigs and liver-lipase of rabbits hydrolyse the  $\text{Me}_2$  ethers of d(+)-(I) and l(−)-(II)  $\alpha$ -butyrylglycerol with a considerable difference in velocity. Triisopropylidenemannitol is hydrolysed to  $\gamma\delta$ -isopropylidene-, m.p. 85—86.5°,  $[\alpha]_D -29.6^\circ$  in  $\text{H}_2\text{O}$ , which with  $\text{Ag}_2\text{O}$  and  $\text{MeI}$  yields  $\alpha\beta\epsilon\zeta$ -tetramethyl- $\gamma\delta$ -isopropylidene-, m.p. 132—134°,  $[\alpha]_D^{20} -39.0^\circ$  in  $\text{H}_2\text{O}$ , and thence  $\alpha\beta\epsilon\zeta$ -tetramethyl-, b.p. 152—157°/9—10 mm.,  $[\alpha]_D +13.2^\circ$  in  $\text{H}_2\text{O}$ , l-mannitol. This is transformed by  $\text{Pb}(\text{OAc})_4$  in  $\text{C}_6\text{H}_6$  at room temp. into dimethyl-l-glyceraldehyde, b.p. 37—42°/8—10 mm., immediately reduced ( $\text{H}_2$ -Raney Ni in  $\text{EtOAc}$  saturated with  $\text{H}_2\text{O}$ ) to l- $\alpha\beta$ -dimethylglycerol, b.p. 65—66°/7 mm.,  $[\alpha]_D +4.8^\circ$  in substance,  $-6.7^\circ$  in  $\text{H}_2\text{O}$ , which with  $\text{Pr}^n\text{COCl}$  in quinoline at room temp. affords (I), b.p. 94.5—95.5°/8 mm.,  $[\alpha]_D +5.9^\circ$ . Similarly obtained are dimethyl-d-glyceraldehyde, b.p. 38.5—39.0°/8 mm.,  $[\alpha]_D +98.0^\circ$  in  $\text{C}_6\text{H}_6$ , d- $\alpha\beta$ -dimethylglycerol, b.p. 67.2—67.4°/8 mm.,  $[\alpha]_D -4.75^\circ$  in substance,  $+6.8^\circ$  in  $\text{H}_2\text{O}$ , and (II), b.p. 93.5—94°/8 mm.,  $[\alpha]_D -6.0^\circ$ . H. W.

**Manufacture of crystalline glycollic acid.**—See B., 1942, II, 357.

**Photosensitised oxidation of ethylenic double bonds.**—See A., 1943, I, 22.

**Preparation of maleic acid.**—See B., 1942, II, 357.

**Production of succinic acid.**—See B., 1942, II, 358.

**Chain photolysis of acetaldehyde in intermittent light.**—See A., 1943, I, 22.

**3 : 2 Compound, m.p. 146—148°, of propaldehyde with acetaldehyde.**—See A., 1942, III, 901.

**Hydration of unsaturated compounds. XI. Acraldehyde and acrylic acid.**—See A., 1943, I, 20.

**Manufacture of keten.**—See B., 1942, II, 358.

**Counting of free alkyl radicals. Application to the photolysis of acetone.**—See A., 1943, I, 22.

**Production of methyl vinyl ketone.**—See B., 1942, II, 388.

**Production of  $\Delta^{\alpha\gamma}$ -hexadien- $\epsilon$ -one.**—See B., 1942, II, 358.

**Formaldehyde-urea condensation products. IV. Methylolureas. V. The methylene linkage.** H. Kadowaki (*Rep. Imp. Ind. Res. Inst., Osaka*, 1933, 14, No. 6, 1—82; 1934, 14, No. 11, 1—87; cf. A., 1936, 868).—IV. The prep. of  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$  (I) [which is converted by aq.  $\text{NH}_3$  into  $\text{CO}(\text{NH}_2)_2$  and  $(\text{CH}_2)_6\text{N}_4$ ] and  $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{OH})_2$  from  $\text{CO}(\text{NH}_2)_2$  and  $\text{CH}_2\text{O}$  in aq. solution is described.

V. The following ethers are described: of (I), *Me*, m.p. 91°, *Et*, m.p. 111°; of dihydroxymethylcarbamide, *Me*, m.p. 101°, *Et*, m.p. 124°, *Pr*, m.p. 95°, *Bu*, m.p. 84°,  $(\text{CH}_2\text{Ph})_2$ , m.p. 112°, and the *Et* thioether, m.p. 108.5°; of methylenedihydroxymethylcarbamide, *Me*, m.p. 240°, *Et*; of dimethyltrimethylenetetra-carbamide, *Me*. The last is hydrolysed to mono- and di-(hydroxymethyl)-trimethylenetetra-carbamide. Peroxides of (I), m.p. 153° (decomp.), and hydroxymethylcarbamide and a related compound, hexahydroxymethyltricarbamide, m.p. 170° (decomp.), are described and the classification of the group as acetals is proposed. CH. Abs. (c)

**Manufacture of diamides of unsaturated carboxylic acids.**—See B., 1942, II, 359.

**Halogenation of unsaturated compounds in the allyl position.** K. Ziegler, A. Späth, E. Schaaf, W. Schumann, and E. Winkelmann (*Annalen*, 1942, 551, 80—119).— $(\text{CH}_2\cdot\text{CO})_2\text{NBr}$  (I) is very suitable for the conversion of  $\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot$  into  $\cdot\text{CHBr}\cdot\text{CH}\cdot\text{CH}\cdot$ . *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{NBr}$  and a large excess of boiling cyclohexene (II) give 50% of 1-bromo- $\Delta^2$ -cyclohexene (III) and 20% of phthal-2-bromocyclohexylimide, m.p. 132—133°. The reaction is greatly retarded when  $\text{CCl}_4$  is used as diluent. *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{NCl}$  and (II) scarcely react in boiling  $\text{CCl}_4$  or  $\text{C}_6\text{H}_6$ ; at 140° 1-chloro- $\Delta^2$ -cyclohexene (IV) results in 12.3% yield but the chief product consists of more highly chlorinated substances with a little additive compound. Halogenated sulphon-amides and -imides are unsuitable. Dichloramine T immediately loses half its active halogen in contact with (II) and the remainder reacts slowly in boiling solution, giving little *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$  and (IV) but mainly a non-cryst. oil. *N*-Chloro-*N*-benzoyl-*p*-toluenesulphonamide, m.p. 59—63°, obtained by the action of  $\text{Ca}(\text{OCl})_2$  on *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NHBz}$  in  $\text{CCl}_4\text{--H}_2\text{O}$  at 0° and (II) give essentially resins. Similar results are obtained with di-*p*-toluenesulphonchloroimide, m.p. 100—102°, obtained by the chlorination of di-*p*-toluenesulphonimide, m.p. 168.5°, derived from *p*- $\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHNa}$  and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  in *o*- $\text{C}_6\text{H}_4\text{Cl}_2$  at 200°. *N*-Chlorosaccharin gives (IV) in 28.3% yield, saccharin, and *N*-2-chlorocyclohexylsaccharin, m.p. 169°. In the presence of  $\text{COMe}_2$  the main product is cyclohexene chlorohydrin. *N*-Bromosaccharin, from Ag saccharin and Br in  $\text{CCl}_4$ , affords *N*-2-bromocyclohexylsaccharin, m.p. 128°, but (III) could not be isolated.  $\text{CCl}_3\cdot\text{CO}\cdot\text{NHCl}$  and (II) in boiling  $\text{CCl}_4$  slowly give (IV) in 14.3% yield and trichloroacet-2-chlorocyclohexylamide, m.p. 84°. *N*-Chloroacylanilides are very useful provided that they are not readily isomerised to nuclear-substituted products. 2 : 4 : 1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NACl}$ , 2 : 4 : 1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NBzCl}$ , 2 : 4 : 1- $\text{C}_6\text{H}_3\text{ClBr}\cdot\text{NACl}$ , 2 : 4 : 1- $\text{C}_6\text{H}_3\text{ClBr}\cdot\text{NBzCl}$ , 4 : 1- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NACl}$ , and 4 : 1- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NACl}$  (V) give ~70—90% of (IV) and ~90% of halogen-free acylanilide. The change does not appear to be influenced by steric hindrance but to be subject to polarisation effects. Steric influences do not appear to control addition. Certain chloroacylanilides such as (V) appear particularly prone to di-substitution. 2 : 4- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NCl}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$  loses its active H fairly readily but gives >50% substitution. To work economically it is necessary to carry out series experiments in which the non-chlorinated excess of substrate is removed and worked up again. Diethylbarbituric acid is transformed by  $\text{Ca}(\text{OCl})_2$  in  $\text{AcOH}$  into the  $\text{NN}'\text{-Cl}_2$ -derivative, m.p. 127.5°, which gives 28.3% of (IV) from (II).  $\text{NN}'\text{N}''$ -Trichlorocyanuric acid and (II) in boiling  $\text{CCl}_4$  give cyanuric acid, (IV) in 29.2% yield, and a non-volatile, resinous residue. The use of  $\text{NHBzCl}$ ,  $\text{NHAcCl}$ ,  $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NCl}$ , and  $(\cdot\text{CO}\cdot\text{NClMe})_2$  is described. Bromination by (I) is usually effected in boiling  $\text{CCl}_4$  (3—4 times the vol. of olefine). Simple olefines of not too small mol. wt. are brominated within 15—60 min., if they contain at least 1  $\text{CH}_2$  vicinal to the double linking. With equiv. amounts the yields are 50—60% and attain 80% in presence of a (recoverable) excess of olefine. The products are homologues of allyl bromide and in suitable cases are homogeneous. The no. of possibilities is limited by the fact that  $\text{CH}_2$  reacts with

(I) almost invariably more rapidly than Me. The following are thus obtained: monobromides from (II),  $\text{CMe}_2\text{CHMe}$ , b.p. 34—40°/15 mm.,  $\beta$ -methyl- $\Delta^8$ -hexene, b.p. 54°/12 mm.;  $\Delta^8$ -octene, b.p. 69°/11 mm., diisobutylene, b.p. 53°/11 mm.;  $\Delta^8$ -nonene, b.p. 99—112°/1 mm., dodecene, b.p. 87°/0.3 mm., and pinene, b.p. 101—109°/12 mm.;  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ , b.p. 84—85°/0.8 mm., from  $\text{CHPh}\cdot\text{CHMe}$ ;  $\gamma\gamma$ -diphenylallyl bromide, b.p. 96—98°/0.5 mm., from  $\text{CPh}_2\cdot\text{CHMe}$ ;  $\gamma$ -bromo- $\alpha\alpha$ -diphenyl- $\Delta^2$ -butene, m.p. 82°, from  $\text{CPh}_2\cdot\text{CHEt}$  (from  $\text{MgPhBr}$  and  $\text{Pr}^n\text{CO}_2\text{Et}$ ). All the Br-compounds give a spontaneous, vigorous reaction when mixed with the double vol. of cyclohexylamine; the change is typical of allyl bromides and is never observed with simple saturated Br-compounds or with homologous vinyl bromides. Substitution at the C:C linking can occur only to a very limited extent and is not generally observed since Br is quantitatively yielded to boiling  $\text{AgNO}_3\text{--EtOH}$ . The allyl bromides are usually readily converted into diolefines by boiling quinoline or collidine, thus further confirming the allyl position of Br. The products contain ~93% of conjugated diene but their constitution is not invariably well defined.  $\Delta^{1:3}$ -cyclohexadiene (VI),  $\beta$ -methyl- $\Delta^8$ -hexadiene, b.p. 107°/760 mm.,  $\Delta^8$ - (or  $\Delta^8$ -)nonadiene, b.p. 85—88°/100 mm., and (?)  $\Delta^{\alpha\gamma}$ -dodecadiene (VII), b.p. 101°/13 mm., m.p. -52°, are thus obtained. (VI) and (VII) are highly resistant to (I); in course of time active halogen disappears and  $(\text{CH}_2\cdot\text{CO})_2\text{NH}$  is formed but  $\text{Br}_1$ -dienes could not be isolated in appreciable amount.  $\text{CH}_2$  in alliance with an open conjugated system is much less reactive than when vicinal to a single unsaturated linking; diolefines are not polymerised in contact with (I). Diolefines with isolated double linking behave normally towards (I); thus  $\beta$ -dimethyl- $\Delta^8$ -dodecadiene, b.p. 88°/12 mm. [from  $\beta$ -dimethyldecane- $\beta$ -diol, m.p. 74° (hydrate, m.p. 53°), through  $\beta$ -chloro- $\beta$ -dimethyldecane- $\alpha$ -ol, m.p. 66°, to  $\beta$ -dichloro- $\beta$ -dimethyldecane, m.p. 26°, which is dehalogenated by boiling quinoline], affords a dibromide which could not be converted satisfactorily into the corresponding tetraene. Polybromination of mono-olefines can be achieved by using a larger proportion of (I) or preferably by the action of (I) on the purified  $\text{Br}_1$ -derivative. 1:4-Dibromo- $\Delta^2$ -cyclohexene, m.p. 108°, and (?)  $\alpha\delta$ -dibromo- $\Delta^8$ -dodecene, b.p. 86°/0.0002 mm., are thus obtained; the last compound is transformed by quinoline into a dodecatriene, b.p. 100—108°/10 mm., m.p. -34°, hydrogenated ( $\text{Pd--BaSO}_4$ ) to dodecane, m.p. -12°. Bromination of (II) in  $\text{CCl}_4$  containing dry  $\text{BzOH}$  gives little (III) but the presence of  $\text{CO}_2\text{H}$  appears sometimes immaterial. Acid anhydrides are permissible and ether groups are not essentially harmful particularly if reaction with highly active  $\text{CH}_2$  is accomplished in  $\text{Et}_2\text{O}$ . cyclohexenyl Et ether behaves obscurely since Br enters in part in place of H neighbouring to OEt. cyclohexenyl acetate readily affords 4-bromocyclohexenyl acetate, b.p. 116—118°/12 mm. Cholesterol is very rapidly substituted. Et undecenoate gives an unidentified  $\text{Br}_1$ -derivative, b.p. 120—126°/0.8 mm., in 46.4% yield. Et oleate yields a reactive  $\text{Br}_1$ -compound which could not be distilled or smoothly transformed into a diene ester.  $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$  reacts slowly under standard conditions, more rapidly with excess of the boiling ester, to yield Me  $\gamma$ -bromocrotonate, b.p. 83—85°/13 mm., hydrolysed to the acid, m.p. 73.5°, which with an excess of alkali gives  $\text{O}(\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H})_2$ , m.p. 195°.  $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}_2\text{Me}$  is much more easily transformed into Me  $\gamma$ -bromo- $\beta$ -methylcrotonate, b.p. 84—89°/12 mm.  $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$  gives black decomp. products but its acetal appears to be brominated.

H. W.

$\alpha$ -Bromopropionylmethionine, m.p. 111.5—112.5° (corr.).—See A., 1942, III, 906.

(A) Polymerisation of acrylonitrile and polyacrylonitrile. (B) Polymerisation of methacrylonitrile and polymethylacrylonitrile. W. Kern and H. Fernow (*J. pr. Chem.*, 1942, [ii], 160, 281—295, 296—314).—(A) Catalytic polymerisation of  $\text{CH}_2\cdot\text{CH}\cdot\text{CN}$  with 1% of  $\text{Bz}_2\text{O}_2$  is examined, and the reaction mechanism is discussed. Under certain conditions of temp. and  $[\text{Bz}_2\text{O}_2]$ , there is some loss of HCN and formation of  $\text{C}_5\text{H}_5\text{N}$ . Polyacrylonitrile (I), decomp. ~350° (99%  $\text{C}_3\text{H}_3\text{N}$  + 1%  $\text{Bz}_2\text{O}_2$ ), and 40% aq. NaOH afford polyacrylic acid. Polymerisation of a mixture of  $\text{CH}_2\cdot\text{CH}\cdot\text{OAc}$ ,  $\text{CHPh}\cdot\text{CH}_2$ , and  $\text{CH}_2\cdot\text{CMe}\cdot\text{CO}_2\text{Me}$  is effected in presence of 5% of  $\text{H}_2\text{O}$ -free HCN and 1% of  $\text{Bz}_2\text{O}_2$  at 50° for 120 hr.

(B)  $\text{CH}_2\cdot\text{CMe}\cdot\text{CN}$  is polymerised in presence of 1—5% of  $\text{Bz}_2\text{O}_2$  at 60° (cf. A., 1936, 1238). The physical properties of polymethylacrylonitrile (II), decomp. ~200° (softens at 115°), are given; warm 40% aq. NaOH converts it into polymethylacrylic acid. Although no pure product is obtained by thermal decomp. of (I), (II) at 250° affords  $\text{CH}_2\cdot\text{CMe}\cdot\text{CN}$ .

A. T. P.

Absorption spectra and X-ray examination of isomeric glucononitriles.—See A., 1942, I, 386.

## II.—SUGARS AND GLUCOSIDES.

Effect of temperature on the validity of Hudson's rules of isomerisation.—See A., 1942, I, 388.

So-called "isosucrose." A. Georg (*Annalen*, 1942, 551, 272—276; cf. A., 1935, 69; Irvine *et al.*, *ibid.*, 1226).—In reply to

Schlubach *et al.* (A., 1942, II, 279) the author maintains the correctness of his hypothesis that isosucrose (I) is  $\beta$ -D-glucopyranosido- $\alpha$ -D-fructofuranoside and not an isoturanose. Account is thereby rendered of the products of hydrolysis, the ease of hydrolysis, and the stability towards Weidenhagen's invertase. Reasons are advanced for considering the reducing power of (I) to differ from that of "normal" reducing disaccharides.

H. W.

Synthesis of 3- $\beta$ -D-glucosidoprotocatechualdehyde and its enzymic fission. B. Helferich and P. Papalambrou (*Annalen*, 1942, 551, 242—248).—3:4:1-(OAc) $\text{C}_6\text{H}_3(\text{OH})\cdot\text{CHO}$  and  $\text{MeSO}_2\text{Cl}$  in  $\text{C}_5\text{H}_5\text{N}$  at 0° yield 4-methanesulphonyl-3-acetylprotocatechualdehyde, m.p. 97°, converted by short warming with  $\text{C}_5\text{H}_5\text{N}$  and  $\text{N-HCl}$  into 4-methanesulphonylprotocatechualdehyde (I), m.p. 127° (p-nitrophenylhydrazone, m.p. 235°), methylated to methanesulphonylvanillin, m.p. 89°, also obtained directly from vanillin and  $\text{MeSO}_2\text{Cl}$ . (I) is transformed by acetobromoglucose and  $\text{N-NaOH}$  in  $\text{COMe}_2$  into 4-methanesulphonyl-3- $\beta$ -D-glucosidoprotocatechualdehyde tetra-acetate, m.p. 172°,  $[\alpha]_D^{25}$  -58° in  $\text{CHCl}_3$  (3-methanesulphonyl-4- $\beta$ -D-glucosidoprotocatechualdehyde tetra-acetate has m.p. 125°,  $[\alpha]_D^{25}$  -40.7° in  $\text{CHCl}_3$ ). This is transformed by controlled alkaline hydrolysis followed by acetylation ( $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  at room temp.) into 3- $\beta$ -D-glucosidoprotocatechualdehyde penta-acetate, m.p. 134—135.5°,  $[\alpha]_D^{18}$  -21.4° in  $\text{CHCl}_3$  (the isomeric penta-acetate has m.p. 120.5°,  $[\alpha]_D^{21}$  -28.8° in  $\text{CHCl}_3$ ), which is hydrolysed to 3- $\beta$ -D-glucosidoprotocatechualdehyde, softens at 125°, m.p. 142—145°,  $[\alpha]_D^{21}$  -103° in acetate buffer (p-nitrophenylhydrazone, m.p. 235°). This is less readily hydrolysed than the isomeric 4-compound by emulsin of sweet almonds.

H. W.

Crystalline cardiac glucoside from *Adonis vernalis*. H. Rosenmund and T. Reichstein (*Pharm. Acta Helv.*, 1942, 17, 176—184).—From 45 g. of the commercial drug prep. "Adovern" there was obtained 18 g. of a  $\text{H}_2\text{O}$ -sol. resin. From this was obtained 6.1 g. of fraction B by partition with  $\text{CHCl}_3$ -96%  $\text{EtOH}$ , whilst the neutral aq. fraction contained 11.5 g. of fraction C. Acetylation of B ( $\text{C}_5\text{H}_5\text{N--Ac}_2\text{O}$ ) and chromatography of the crude product yielded an acetate of the active cardiac glucoside, m.p. 146—148°,  $[\alpha]_D^{16}$  -56.5°  $\pm$  2° in  $\text{CHCl}_3$  [free glucoside, m.p. 263—265° (decomp.),  $[\alpha]_D^{16}$  -27° in  $\text{MeOH}$ ], and an acetate, m.p. 237—238° (decomp.),  $[\alpha]_D^{14}$  +30.4°  $\pm$  3° in  $\text{CHCl}_3$ , hydrolysed to a substance, m.p. 238—240° (decomp.),  $[\alpha]_D^{15}$  +53  $\pm$  2° in  $\text{EtOH}$ , the lower biological activity of which corresponded more with that of a genin. Chromatography of the crude product of acetylation of C yielded acetate 1, m.p. 122—124°, acetate 2, m.p. 59—60°,  $[\alpha]_D^{16}$  +147°  $\pm$  3° in  $\text{COMe}_2$ , from which a cryst. compound could not be isolated by hydrolysis with  $\text{Ba}(\text{OH})_2\text{--MeOH}$ , and an amorphous fraction from which adonitol, m.p. 102—104°, was isolated after hydrolysis with  $\text{KHCO}_3$  in aq.  $\text{MeOH}$ .

P. G. M.

Composition of the eriodictyol glycoside. A. Mager (*Z. physiol. Chem.*, 1942, 274, 109—115).—The eriodictyol glycoside, m.p. 184—186° (much decomp.),  $[\alpha]_D^{20}$  -51.53° in  $\text{C}_5\text{H}_5\text{N}$ , is isolated from citrin by chromatography over  $\text{Al}_2\text{O}_3$ . It is hydrolysed by 1%  $\text{H}_2\text{SO}_4$  to eriodictyol, m.p. 258—260° (decomp.), and rhamnose, identified as the phenylosazone, m.p. 186—187° (decomp.).

H. W.

Hemicelluloses and pectic material from cottonwood.—See A., 1942, III, 950.

## III.—HOMOCYCLIC.

Chlorination of benzene.—See B., 1942, II, 359.

Binary systems composed of titanium tetrachloride and nitrocompounds. N. A. Pushin, L. Nikolić, A. Radojčin, and T. Uroponova (*Annalen*, 1942, 551, 259—271).—The m.p. diagrams show that  $\text{TiCl}_4$  forms well-defined equimol. compounds with  $\text{PhNO}_2$ , *m*- and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ , *m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$ , *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ , and 1:2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$  with respective crystallisation temp. 75°, 61°, 54.5°, 72°, 62.5°, 75°, 72.3°, and 64°.  $\text{TiCl}_4$  and *m*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$  give a 1:1 and probably a 2:1 compound; with 1:3:5- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$  the corresponding 1:1 and 2:1 substances crystallise at 43° and 46°, respectively.  $\text{TiCl}_4$  and 1:2:4:6- $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$  do not form a compound and do not always mix completely in the liquid phase.

H. W.

Mechanism of the thermal polymerisation of styrene.—See A., 1943, I, 19.

Occurrence of free radicals in chemical reactions. X. Aromatic diacyl peroxides and triphenylmethyl. H. Wieland and A. Meyer (*Annalen*, 1942, 551, 249—258; cf. A., 1937, II, 498).—Evidence is adduced in favour of the view that the fourth Ph of  $\text{CPh}_4$  obtained in small proportion by the interaction of  $\text{Bz}_2\text{O}_2$  and  $\text{CPh}_3$  in  $\text{C}_6\text{H}_6$  is derived from the solvent. Gradual introduction of 4N-NaOH into the solution obtained by addition of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COCl}$  in  $\text{COMe}_2$  to a mixture of 30%  $\text{H}_2\text{O}_2$  and  $\text{COMe}_2$  gives di-*p*-tolyl peroxide (I), m.p. 143—144° (much decomp.), which with  $\text{CPh}_3$  in  $\text{PhMe}$  affords  $\text{CPh}_3$  *p*-toluate, m.p. 187—189° (obtained also from *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{Ag}$  and  $\text{CPh}_3\text{Cl}$ ), and triphenyl-*p*-tolylmethane (II), m.p. 163°. (I) and  $\text{CPh}_3$  in  $\text{PhCl}$  yield chlorotetraphenylmethane, m.p. 194°, and in  $\text{MeOBz}$  give Me tetraphenylmethane-*p*-carboxylate, m.p. 135°. (II)

is oxidised by  $\text{SeO}_2$  at  $220^\circ$  and then at  $320^\circ$  to *tetraphenylmethane-p-carboxylic acid*, m.p.  $214^\circ$ , decarboxylated to  $\text{CPh}_4$ , m.p.  $274-275^\circ$ . ( $p\text{-OMe}\cdot\text{C}_6\text{H}_4$ ) $_2\text{O}_2$  and  $\text{CPh}_3$  in  $\text{C}_6\text{H}_6$  afford  $\text{CPh}_4$ , with  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  and  $\text{CPh}_3\cdot\text{OH}$  which result from the ready hydrolysis of  $\text{CPh}_3$  anisate, m.p.  $164^\circ$ . ( $p\text{-C}_6\text{H}_4\text{Me}$ ) $_2\text{O}_2$  and  $\text{C}(\text{C}_6\text{H}_4\text{Me-}p)_3$  in  $\text{PhMe}$  afford *tetra-p-tolylmethane*, m.p.  $130^\circ$ . *cyclohexyltriphenylmethane*, m.p.  $143-145^\circ$ , is derived from  $\text{Bz}_2\text{O}_2$  and  $\text{CPh}_3$  in cyclohexane. H. W.

**Tri-o-tolylmethane.** P. D. Bartlett and J. E. Jones (*J. Amer. Chem. Soc.*, 1942, 64, 1837—1842).—*Tri-o-tolylmethane* (I), m.p.  $130.5-131.5^\circ$  after sintering at  $\sim 126^\circ$ , differs from its homologues in giving with  $\text{CPhMe}_2\text{K}$  in  $\text{Et}_2\text{O-N}_2$  at room temp. in absence of light an insol.  $\text{K}_3$  salt,  $\text{CH}(\text{C}_6\text{H}_4\text{-CH}_2\text{K-o})_3$ , converted by  $\text{CO}_2$  into *tri-(o-carboxymethylphenyl)methane* (II) (98.3%), m.p.  $265-295^\circ$  (decomp.; block; gradual heating),  $\leq 310^\circ$  (later decomp.; block; immediate), and  $\text{PhPr}^\beta$  (86%). The structure of (II) is proved by formation of a  $\text{Et}_3$  ester, m.p.  $196.5-197.5^\circ$ , by  $\text{HCl-EtOH}$  and by stability in conc.  $\text{H}_2\text{SO}_4$  at  $100^\circ$ . Homologues form salts,  $\text{CAr}_3\text{K}$ , but  $\text{CHPh}(\text{C}_6\text{H}_4\text{Me-o})_2$  (III) is intermediate, giving with 0.059N- $\text{CPhMe}_2\text{K}$  and later  $\text{CO}_2$  86% of *phenyldi-o-tolylacetic*, m.p.  $184-185^\circ$  (in  $\text{H}_2\text{SO}_4$  at  $100^\circ$  gives  $\text{CO}$ ), and 8.6% of *phenyl-o-tolyl-o-carboxymethylphenylacetic acid* (IV), m.p.  $265-257^\circ$  (decomp.) ( $\text{Me}_2$  ester, m.p.  $105-106^\circ$ , prepared by  $\text{MeOH-HCl}$ ; gives no  $\text{CO}$  in  $\text{H}_2\text{SO}_4$ ); 0.107N-(III) and 0.083N- $\text{CPhMe}_2\text{K}$  give 39% of (IV). Explanations of the differences by means of damped resonance and steric hindrance are discussed. *Di-o-tolylphthalide* [prep. from  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$  and  $o\text{-C}_6\text{H}_4\text{Me-MgBr}$  in  $\text{Et}_2\text{O-C}_6\text{H}_6$ ; 61.5% yield] and  $\text{H}_2\text{-Cu}$  chromite at  $235-250^\circ/2325$  lb. give 2:2'-*dimethyltriphenylmethane-2''-carboxylic acid* (70—83%), m.p.  $241-242^\circ$  (in one experiment in dioxan, 51% with 2.8% of a neutral substance, m.p.  $145.4-146^\circ$ ), converted by  $\text{PCl}_5\text{-C}_6\text{H}_6$  and then  $\text{NH}_3\text{Ph}$  into the *anilide*, m.p.  $164.0-164.7^\circ$ . With  $\text{PCl}_5\text{-PhMe}$  at room temp. and later  $100^\circ$  and then  $\text{SnCl}_4\text{-HCl-Et}_2\text{O}$  at  $0^\circ$  this gives *di-o-tolyl-o'-aldehydophenylmethane* (44%), sinters at  $131^\circ$ , m.p.  $134.5-135^\circ$  (*oxime*, m.p.  $174.8-175.2^\circ$ ; impure *semicarbazone*, m.p.  $208.5-209.5^\circ$ ), which with  $\text{NaOEt-EtOH-85\% N}_2\text{H}_4\cdot\text{H}_2\text{O}$  (no hydrazone isolated) at  $200-210^\circ$  gives 83% of (I). The m.p. of (I) is much depressed by impurities. Interaction of  $o\text{-C}_6\text{H}_4\text{Me-MgBr}$  with  $\text{COPh}_2$  in  $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ , decomp. by dil.  $\text{H}_2\text{SO}_4$ , and heating the product with 85%  $\text{HCO}_2\text{H}$  gives  $\text{CHPh}_2\cdot\text{C}_6\text{H}_4\text{Me-o}$  (V) (53%), m.p.  $81-83^\circ$ ; use of  $\text{EtOBz}$  instead of  $\text{COPh}_2$  gives similarly (III) (45%), m.p.  $102-104^\circ$ . With  $\text{CPhMe}_2\text{K}$ , (V) gives 98.7% of  $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ , m.p.  $228-229^\circ$  or  $190-200^\circ$  (block; decomp.), converted in conc.  $\text{H}_2\text{SO}_4$  at  $50^\circ$  into  $\text{CO}$  and  $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{CPh}_2\cdot\text{OH}$  (82.5%), m.p.  $98-99^\circ$  (lit.  $98^\circ$ ). ( $p\text{-C}_6\text{H}_4\text{Me}$ ) $_3\text{CH}$ , b.p.  $232^\circ/11$  mm., gives similarly 73.5% of ( $p\text{-C}_6\text{H}_4\text{Me}$ ) $_3\text{C}\cdot\text{CO}_2\text{H}$  and thence ( $p\text{-C}_6\text{H}_4\text{Me}$ ) $_3\text{C}\cdot\text{OH}$ . M.p.  $<230^\circ$  are corr. R. S. C.

**"Tervalent" carbon. XVI. A much discussed radical-chemical problem and its final solution.** K. Ziegler (*Annalen*, 1942, 551, 127—149).—Evidence is adduced from the literature against Hückel's dictum that a dimeride has never been certainly obtained from radicals in which one substituent is of aliphatic nature and that these radicals become altered largely at any rate in another manner. All evidence points in the same direction that substituted ethanes of this type exist which can dissociate spontaneously into radicals. Further it is shown that the rate of autoxidation in presence of pyrogallol of many not exclusively aromatic-substituted ethanes [*tetraphenyl-dimethyl-* (I), *-diethyl-* (II), *-dipropyl-*, *-diisopropyl-* (III), *-di-n-butyl-*, *-ditert.-butyl-*, *-di-n-amyl-*, and *-dicyclohexyl-ethane*] follows exactly the same laws as that of  $\text{C}_2\text{Ph}_6$ ; hence it must be assumed that these compounds behave similarly to  $\text{C}_2\text{Ph}_6$  and therefore decompose spontaneously into radicals. The only exceptional compound is *di-9-phenylfluorenyl*. Additional evidence in the same direction is afforded by the isolation of  $\text{CPh}_2\text{Me}\cdot\text{O}_2\text{H}$  and  $\text{CPh}_2\text{Et}\cdot\text{O}_2\text{H}$  in the cryst. condition by the autoxidation of  $(\text{CPh}_2\text{Me})_2$  and  $(\text{CPh}_2\text{Et})_2$  with  $\text{O}_2$  in presence of pyrogallol. Autoxidation of  $\text{C}_2\text{Ph}_6$  in presence of foreign  $\text{O}_2$ -acceptors may be accompanied by chain reactions in which  $\text{CPh}_3$  functions as a very efficient  $\text{O}_2$ -carrier. This phenomenon can be utilised for the detection of very slight dissociation since it causes great multiplication of what, in absence of acceptor, may be a very small  $\text{O}_2$  absorption. The reaction is strongly positive with all the ethanes described above and since these are employed solely in the colourless, cryst. ethane forms their true radical dissociation is established. Observation of the disproportionating decomp. of (I), (II), and (III) shows that this takes place with certainty through radicals and is caused by two radicals in contact exchanging a H atom between one another; with (I), (II), and (III) respectively this takes place 10, 100, and  $\sim 3500$  times more slowly than radical formation. Hence with these ethanes in absence of  $\text{O}_2$  the dissociation equilibria must be established almost without hindrance. It is remarkable that no marked colour of the solution is observable with these and similar compounds at temp. at which the decomp. consts. are similar to those of  $\text{C}_2\text{Ph}_6$ . This may be due to a much greater rate of re-association or to the feeble colour of the radicals. *Tetracyclohexyldiphenylethane* is obtained as a colourless cryst. compound which towards  $\text{O}_2$  and pyrogallol behaves in the same manner as  $\text{C}_2\text{Ph}_6$ ;  $\text{O}_2$  is gradually absorbed as the ethane decom-

poses and the criteria of "indirect" oxidation through a radical (change of the first order independent of  $\text{O}_2$  pressure) are fulfilled. The existence of *dicyclohexylphenylmethyl H peroxide* is rendered probable and the autoxidation of unsaturated acceptors (*cyclohexadiene* and *styrene*) is shown to be greatly accelerated by the ethane. There is no evidence of the particularly marked retardation of the association of *dicyclohexylphenylmethyl* as postulated by Hückel. Complete hydrogenation of 2 Ph groups of  $\text{C}_2\text{Ph}_6$  diminishes the rate of dissociation in the ratio 170:1 whilst complete hydrogenation of 2 additional Ph groups does not cause much further change. An explanation of the causes of radical dissociation is sought in a combination of Hückel's theory with the author's hypothesis of the dilatation of the central linking by *cyclohexyl*. H. W.

**"Tervalent" carbon. XVII. Kinetics and energetics of radical dissociations.** K. Ziegler, A. Seib, K. Knoevenagel, P. Herte, and F. Andreas (*Annalen*, 1942, 551, 150—186).—Improved methods have been devised for the measurement of the rate of absorption of  $\text{O}_2$  by solutions of substituted ethanes or their radicals. An essential for the application of the method is an adequate concn. of pyrogallol and as great a dilution of the ethane as is possible. The correctness of conditions is recognised by the independence of the reaction const. on the  $\text{O}_2$  pressure and the strict fulfilment of the requirements for a change of the first order. The absorption of  $\text{O}_2$  by  $\text{C}_2\text{Ph}_6$  in a wide variety of solvents has been measured; the consts. thus obtained agree well with those recorded for absorption of  $\text{NO}$  and those determined with I in  $\text{CHCl}_3$  (cf. Ziegler *et al.*, A., 1933, 943). The influence of solvent on the const. is remarkably small. Comparison of the rates of dissociation of  $\text{C}_2\text{Ph}_6$ , *diphenyltetradiphenyl-* and *tetraphenyldidiphenyl-ethane* in  $\text{CH}_2(\text{CO}_2\text{Et})_2$  shows that the influence of the *p*-Ph group is not particularly marked. Decomp. consts. ( $K$ ), half life periods ( $\tau$ ), energy of activation ( $E$ ), and temp.-controlled factors ( $a$ ) are measured for many *tetraphenyldialkylethanes* in  $\text{PhBr}$  over an interval of  $40^\circ$ . In these respects  $(\text{CPh}_2\text{Me})_2$  is much more closely allied to  $\text{C}_2\text{Ph}_6$  than to its higher homologues. The latter containing *n*-alkyl groups form a class by themselves with characteristic  $E$  and  $a$  and possibly without a marked influence of the length of the alkyl chain. Those containing *isoalkyl* residues also form a well-marked group which dissociate much less rapidly than the *n*-alkyl class due mainly to much smaller vals. of  $a$ . *Dimethyl-*, *diethyl-*, *di-n-propyl-*, and *di-n-butyl-dixanthyl* have almost the same vals. of  $E$  and  $a$  and form a well-marked group in which the first named compound does not occupy a unique position. In general, the authors' results are not in harmony with the theoretical considerations of Polanyi *et al.* (A., 1929, 404), the apparent agreement noted by Salomon (A., 1934, 44) being fortuitous. From the viewpoint of energy of activation the *di-n-alkyldixanthyls* and  $(\text{CPh}_2\text{Me})_2$  are equiv., the strongly polarising entry of the 2 oxido-O atoms into the aromatic nucleus having no apparent effect on the firmness of the C-C linking. Comparison of the higher *tetraphenyldialkylethanes* with the *dixanthyls* shows that the 2 O cause a distinct increase in the firmness of the central linking. *sec.* Substituents cause a weakening of the attachment of substituted methyls, shown by a lowering of the activation energy by  $\sim 2$  kg.-cal. The absorption of  $\text{O}_2$  by *di-9-phenylfluorenyl* is a change of the first order but the reaction const. is greatly dependent on the  $\text{O}_2$  pressure; in presence of pyrogallol the rate of the total reaction is somewhat diminished but its dependence on the pressure of  $\text{O}_2$  is scarcely affected. This unique behaviour is attributed to an increased tendency towards association. *Diphenyltetra(diphenyl)ethane* is best prepared by the reduction by  $\text{CrCl}_2$  of *phenyldidiphenylcarbinol* in  $\text{COMe}_2$  containing  $\text{HCl}$ . *Diphenyl-n-propylcarbinol Me ether*, m.p.  $90^\circ$ , is converted by  $\text{Na-K}$  followed by  $(\text{CMe}_2\text{Br})_2$  into *tetraphenyldi-n-propylethane*, m.p.  $70^\circ$  (under  $\text{N}_2$ ).  $\text{Bu}^n\text{CO}_2\text{Et}$  and  $\text{MgPhBr}$  yield *diphenyl-n-butylcarbinol*, b.p.  $135-140^\circ/0.2$  mm., transformed through the *Me ether*, m.p.  $47^\circ$ , into *tetraphenyldi-n-butylethane*, m.p.  $62-63^\circ$  (under air),  $68-70^\circ$  (under  $\text{N}_2$ ). Similarly obtained are *diphenyl-n-amylcarbinol*, m.p.  $46-47^\circ$ , its *Me ether*, m.p.  $55-57^\circ$ , and *tetraphenyldi-n-amylethane*, which could not be crystallised. *Tetraphenyldiisopropylethane* has m.p.  $140-141^\circ$  (under  $\text{N}_2$ ). *Diphenyltert.-butylcarbinol Me ether*, b.p.  $172-173^\circ/13$  mm., m.p.  $45^\circ$ , is described. *cyclopentyldiphenylcarbinol* (I), m.p.  $44^\circ$  (lit.  $112^\circ$ ), obtained from *Me cyclopentanecarboxylate* and  $\text{MgPhBr}$  or from  $\text{COPh}_2$ , *cyclopentyl bromide*, and  $\text{Na}$ , gives a *Me ether*, b.p.  $100-105^\circ/0.001$  mm., and thence *dicyclopentyldiphenylethane*, m.p.  $117-119^\circ$  (under  $\text{N}_2$ ),  $87-89^\circ$  (under air). The following are described incidentally: *cyclopentyldiphenylacetic acid*, m.p.  $161-162^\circ$ , from the K compound and  $\text{CO}_2$ ; *cyclopentyldiphenylmethane*, b.p.  $126^\circ/15$  mm., m.p.  $32-33^\circ$ , from the K compound and  $\text{H}_2\text{O}$  or by dehydration ( $\text{AcOH-H}_2\text{SO}_4$ ) of (I) to *cyclopentylidenediphenylmethane*, m.p.  $62-63^\circ$ , which is hydrogenated. H. W.

**"Tervalent" carbon. XVIII. Mechanism of a disproportionation.** K. Ziegler, R. B. Whitney, and P. Herte (*Annalen*, 1942, 551, 187—205).—The "disproportionating" decomp. of  $(\text{CPh}_2\text{Me})_2$ ,  $(\text{CPh}_2\text{Et})_2$ , and  $(\text{CPh}_2\text{Pr}^\beta)_2$  occurs more slowly than the radical dissociation. Attempts to measure the rate of decomp. by titration of the unsaturated compounds produced by means of  $\text{Br}$  or  $\text{ICl}$  are

not sufficiently accurate and the process is followed interferometrically in PhBr at various temp. The reaction is of the first order, thus excluding the possibility that the ethane is in dissociation-association equilibrium with the radicals one of which stabilises itself by unimol. loss of active H which is absorbed by the other radical with immeasurable rapidity. The remaining possibilities are (A) that the ethane is in equilibrium with the radical and that disproportionation occurs in true interaction of two radicals, and (B) that the ethane is in equilibrium with the radical but the products of disproportionation are formed by a direct decomp. of the ethane portion and, also, a (small) proportion of the radical becomes disproportionated through the ethane. Decision in favour of (A) is reached by a study of the autoxidation of  $(CPh_2Me)_2$  in very dil. solution in PhCl containing pyrogallol.  $CPh_2\cdot CH_2$  in the product is transformed by  $CPhMe_2K$  into  $CPh_2K\cdot CH_2\cdot CPhMe_2$ , which is converted by  $CO_2$  into the non-volatile  $CO_2H\cdot CPh_2\cdot CH_2\cdot CPhMe_2$ , leaving  $CHPhMe$  as the only possible volatile compound. This can be readily detected by slow reaction with  $CPhMe_2K$  to  $CPh_2MeK$  and thence to  $CPh_2Me\cdot CO_2H$ . It cannot, however, be found thus in the reaction products. Disproportionation therefore is caused by the direct exchange of H between two radicals in contact and an independent direct disproportionating decomp. of tetraphenyl-dialkylethanes is not encountered. H. W.

**"Tervalent" carbon. XIX. Radical hydrogen peroxides; pyrogallol as antioxidant.** K. Ziegler and P. Herte (*Annalen*, 1942, 551, 206—212).—Gradual addition of solid  $(CPh_2Me)_2$  to PhCl containing pyrogallol (I) through which  $O_2$  is passing at  $80^\circ$  gives *aa-diphenylethyl H peroxide* (II), m.p.  $86^\circ$ , in 70% yield. (II) can be sublimed unchanged at  $70\text{--}75^\circ$ /high vac. and is stable at its m.p. but commences to decompose at  $160^\circ$  in a complex manner. It sometimes inflames when brought in contact with conc.  $H_2SO_4$ , is stable towards warm alkali hydroxide, and liberates I from KI particularly rapidly in presence of AcOH. With boiling  $H_2O$  it affords  $H_2O_2$  and  $CPh_2Me\cdot OH$ , also obtained by treating (II) with excess of  $MgPhBr$ . The free H of (II) has no marked acidic properties but (II) is converted by  $CPh_3Cl$  and alkali into  $CPh_3$  *aa-diphenylethyl peroxide*, m.p.  $126\text{--}127^\circ$ . *aa-Diphenylpropyl H peroxide*, m.p.  $81\text{--}82^\circ$ , is obtained similarly from  $(CPh_2Et)_2$ . Loss of H converts (I) into complex, sparingly sol. and difficultly volatile substances. H. W.

**"Tervalent" carbon. XX. Radicals as catalysts as autoxidation.** K. Ziegler and K. Gänicke (*Annalen*, 1942, 551, 213—221; cf. A., 1933, 943).—Further purification of benzodimethylfulvene (I) has not led to the formation of reaction chains with  $>55,000$  members in autoxidations catalysed by  $CPh_3$ , possibly owing to the formation of compounds between  $CPh_3$  and the unsaturated acceptor. The difference in the activity of  $(CPh_2Me)_2$  and  $(CPh_2Et)_2$  towards the absorption of  $O_2$  by (I) is exactly as would be expected from the great difference in their half-life periods (6600 : 1). Dicyclohexyl-tetraphenylethane (II) is a potent  $O_2$ -carrier giving a chain with  $\sim 2000$  links and thus comparable with that of  $C_2Ph_4$  and (I) which has not been purified with particular care. The catalytic activity of (II) in  $CHCl_3$  is practically non-existent after 143 hr. at  $20^\circ$ . The catalytic activity of dimethyl-, diethyl-, and dibutyl- (III)-dixanthyl is  $<$  that of (II); (III) is the most active of the three compounds. Free substituted-methyl radicals can function universally as autoxidation catalysts. Conversely in doubtful cases the incidence of catalytic activity may be regarded as a proof of radical dissociation. In presence of (I) and  $CPh_3$  and under conditions which cause  $\sim 1200\text{--}1500$  links in the reaction chain of the undisturbed system there is a reduction to  $\sim 500$  links in the presence of m./50,000 pyrogallol (IV) and to  $\sim 15$  links when (I) and (IV) are in equiv. proportions. Amongst compounds which can yield H (IV) is by far the most active.  $PhOH$ ,  $m\text{-}C_6H_4(OH)_2$ , and  $\alpha\text{-}C_{10}H_7\cdot OH$  have approx. equal activity whereas guaiacol and  $\beta\text{-}C_{10}H_7\cdot OH$  are less potent. Freshly distilled pyrrole is not an inhibitor and does not function as  $O_2$ -acceptor. If preserved for a few hr. under  $N_2$  it becomes slightly yellow and then behaves as a powerful antioxidant.  $PhSH$  behaves by itself and in conjunction with  $CPh_3$  as a powerful catalyst of autoxidation.  $Ph_2S_2$  does not accelerate the autoxidation of (I) with or without  $CPh_3$  and does not influence the chain reactions. It is not therefore causative of the action of  $PhSH$ . H. W.

**Purification of anthracene, phenanthrene, and carbazole.**—See B., 1942, II, 359.

**Simplified preparation of rubrene.** G. Wittig and D. Waldi (*J. pr. Chem.*, 1942, 160, [ii], 242—244).— $CHPh:CHBr$  and  $LiPh$  in  $Et_2O$  ( $N_2$ ), followed by  $COPh_2\text{-}Et_2O$ , afford *aa $\gamma$ -triphenyl- $\Delta^8$ -propinen- $\alpha$ -ol*, m.p.  $81\text{--}82^\circ$ , converted by  $SOCl_2$  at  $-10^\circ$  into the corresponding chloride, which with 2% of quinoline at  $120^\circ$  in vac. yields rubrene, m.p.  $332^\circ$ . A. T. P.

**H. Wieland's work on nitrogenous substances.** F. Klages (*Naturwiss.*, 1942, 30, 351—359).—A review. F. O. H.

**Organo-boron-nitrogen compounds. II. Reaction of boron chloride with *p*-toluidine.** C. R. Kinney and M. J. Kolbezen (*J. Amer. Chem. Soc.*, 1942, 64, 1584—1585; cf. A., 1939, II, 460).—Addition

of  $p\text{-}C_6H_4Me\cdot NH_2$  (I) in  $C_6H_6$  to  $BCl_3\text{-}C_6H_6$  at  $0^\circ$  gives the 1 : 1 salt (95.4%) (II), m.p.  $159\text{--}160^\circ$  (loses  $HCl$ ), which in boiling  $C_6H_6$  (or at the m.p.) gives 2  $HCl$  and "trichloro-*p*-tolylboron nitride" (III),  $NX\langle\begin{smallmatrix} BCl\cdot NX \\ BCl\cdot NX \end{smallmatrix}\rangle BCl$  ( $X = p\text{-tolyl}$ ),  $+C_6H_6$ , softens at  $304^\circ$ , m.p.  $308\text{--}309^\circ$  (darkens). In cold  $H_2O$ , (III) gives  $p\text{-}C_6H_4Me\cdot NH_2\cdot HCl$  and  $H_3BO_3$ .  $BCl_3$  and an excess of (I) in  $C_6H_6$  at  $110^\circ$  (bath) give *B tri-*p*-toluidide* (35%),  $B(NH\text{-}C_6H_4Me\text{-}p)_3$ , m.p.  $165\text{--}166^\circ$ , unstable in air or  $H_2O$ , and reconverted by  $HCl\text{-}C_6H_6$  into (II) and  $C_6H_4Me\cdot NH_2\cdot HCl$ . R. S. C.

**Associating effect of the hydrogen atom. XI. Hydrogen bonds involving the sulphur atom. The S-H-N bond.** G. Hopkins and L. Hunter (*J.C.S.*, 1942, 638—642; cf. A., 1942, II, 63).—Thioamides possessing the group  $-NH\cdot CS-$  are associated by virtue of intermol. S-H-N linkings. Replacement of imino-H, or its engagement in chelate ring formation, prevents association by rendering such bonds impossible. Although  $CSMe\cdot NPh$  (I) shows a high degree of association, *thioacet-o-nitroanilide*, m.p.  $109^\circ$ , *Me thioacet-anthranilate*, m.p.  $110\text{--}111^\circ$ , and *2-thioacetamido-5 : 4'-dimethylazobenzene*, m.p.  $137\text{--}139^\circ$ , are substantially unimol., since intramol. co-ordination of the anilido-H renders it non-available for intermol. co-ordination. Isomerides or analogues of these compounds with *m*- or *p*-substituents, i.e., donor groups too far removed to involve anilido-H chelation, are as highly associated as (I). Mol. wt. measurements show that 2-thiolbenzthiazole, m.p.  $179^\circ$ , is highly associated (the cyclic S probably plays no part in association), whereas 2-methylthiolbenzthiazole, m.p.  $49^\circ$ , is unimol. 2-Methylbenzthiazole is completely unassociated, as there is no tautomeric H available; 2-anilinobenzthiazole is strongly associated, due to amidine association (*loc. cit.*). The unimol. state of thiodiphenylamine (does not form a S-H-N bond) supports the view that only H capable of tautomeric transfer will take part in S-H-N linkings. Thioacridone shows high association in  $PhNO_2$ , whereas its S-Me and S-Bz derivatives are unassociated (in  $C_6H_6$ ). Thioacridone is considered to have a chain-polymeric structure in which the mol. units are joined by S-H-N linkings between CS and NH of adjacent mols. Derivatives of  $HCS\cdot NH_2$  show abnormal association not necessarily dependent on H bonds.  $HCS\cdot NMe_2$  is highly associated in  $C_6H_6$  solution. The following are prepared from  $RCO\cdot NHR'$  and  $P_2S_5$  in boiling xylene: *thioacet-m-*, m.p.  $98^\circ$ , and *-p-nitroanilide*, m.p.  $175^\circ$ , *-m-*, m.p.  $64^\circ$ , and *-p-toluidide*, m.p.  $52\text{--}53^\circ$  (*o*-isomeride has m.p.  $66^\circ$ ), *-ethylanilide*, m.p.  $49^\circ$ , and *-benzylanilide*, m.p.  $82\text{--}83^\circ$ ; *thiobenzbenzylanilide*, m.p.  $119\text{--}120^\circ$ ; *Et p-thioacetamidobenzoate*, m.p.  $98^\circ$ ; *p-thioacetamidoazobenzene*, m.p.  $143\text{--}144^\circ$ . A. T. P.

**Maleanils.**—See B., 1942, II, 422.

**N-Diphenylloxamic acids.**—See B., 1942, II, 423.

**Sulphanilamides and experimental tuberculosis.** B. Sjögren (*Nature*, 1942, 150, 431—432).—2-Sulphanilamido-1 : 4-naphthoquinone, m.p.  $227^\circ$ , 1-sulphanilamido-2-methylnaphthalene, m.p.  $248^\circ$ , and 4-sulphanilamido-2-methyl-1-naphthol, m.p.  $209^\circ$  (decomp.), have been prepared. They are all more or less sol. in fat solvents and insol. in water. (Cf. A., 1943, III, 49.) E. R. S.

**Mechanism of the diazo-coupling reaction.** H. H. Hodgson (*J. Soc. Dyers and Col.*, 1942, 58, 228—231).—For all coupling reactions, whether in acid, neutral, or alkaline media, the condensation of undissociated but polarised (cationoid)  $NAr\cdot NX$  ( $X = OH, OAc, Cl, HSO_4$ , etc.) with amines or phenols (anionoid) at a polarised C-H linking is the most probable explanation of the known data. Other mechanisms (*lit.*) are criticised. A. T. P.

**Masking of phenolic hydroxyl groups by esterification with methanesulphonic acid.** B. Helferich and P. Papalambrou (*Annalen*, 1942, 551, 235—241).—Phenols are transformed by  $MeSO_2Cl$  (I) into methanesulphonates which, even when sol. in  $H_2O$ , are scarcely affected by prolonged boiling with conc.  $HCl$  but are hydrolysed by *N*-alkali in aq.  $COMe_2$  at room temp. With completely esterified polyhydric phenols the removal of 1  $MeSO_2$  is still more easily effected but more drastic treatment is required for removal of the remainder.  $MeSO_2Ph$ , m.p.  $59\text{--}61^\circ$ , is obtained from  $PhOH$  and (I) in anhyd.  $C_6H_6$  at room temp., or by dropwise addition of (I) (alone or in  $C_6H_6$ ) to  $PhOH$  in aq.  $KOH$  at  $0^\circ$ . The following are new:  $\beta\text{-}C_{10}H_7$ , *methanesulphonate*, m.p.  $105^\circ$ ; *dimethanesulphonates* of *o*-, *m*-, and *p*- $C_6H_4(OH)_2$ , m.p.  $104\text{--}105^\circ$ ,  $87^\circ$ , and  $167^\circ$ , respectively; *trimethanesulphonates* of 1 : 3 : 5-, 1 : 2 : 3-, and 1 : 2 : 4- $C_6H_3(OH)_3$ , m.p.  $149\text{--}5^\circ$ ,  $159^\circ$ , and  $115^\circ$ , respectively; *alizarin dimethanesulphonate*, m.p.  $210^\circ$ ; *quinol monomethanesulphonate*, m.p.  $76^\circ$ ; *phloroglucinol mono- and di-methanesulphonate*, m.p.  $130\text{--}5^\circ$  and  $118^\circ$ , respectively. H. W.

**Phosphoric acid esters of substituted quinols.**—See B., 1942, III, 277.

**Synthetic, highly active oestrogens.** W. Salzer (*Z. physiol. Chem.*, 1942, 274, 39—47).— $p\text{-}OMe\text{-}C_6H_4\cdot CH_2Ac$  (I),  $m\text{-}OMe\text{-}C_6H_4\cdot [CH_2]_2Br$  (II), and  $NaNH_2$  in boiling  $Et_2O$  afford  $\alpha\text{-}p\text{-anisyl-}\gamma\text{-}m\text{-anisylpropyl Me ketone}$ , b.p.  $175^\circ/0.5\text{ mm.}$ , cyclised by 80%  $H_2SO_4$  at  $60\text{--}70^\circ$  to 6-methoxy-2-*p*-anisyl-1-methyl-3 : 4-dihydronaphthalene, m.p.  $136^\circ$ ;

this is demethylated by KOH-EtOH at 200° to (?) 6-hydroxy-2-*p*-hydroxyphenyl-1-methyl-3:4-dihydronaphthalene (III), m.p. 193°, accompanied by (?) 6-methoxy-2-*p*-hydroxyphenyl-1-methylnaphthalene, m.p. 215°, and by MgMeI at 180° solely to (III). Similarly, (I), *m*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>Cl, and powdered NaNH<sub>2</sub> in boiling Et<sub>2</sub>O yield *α*-*p*-anisyl-β-*m*-anisylethyl Me ketone, b.p. 175°/0.5 mm., cyclised to 5-methoxy-2-*p*-anisyl-1-methylindene, m.p. 110°, which is demethylated (KOH-MeOH at 200°) to the 5-hydroxy-2-*p*-hydroxyphenyl derivative (IV), identified as its diacetate, m.p. 131°. Hydrogenation of (IV) gives a non-cryst. phenolic product (V) which does not yield cryst. derivatives. (III) and (IV) are physiologically active in doses of 0.3–0.5 μg. whereas (V) is inactive in a dose of 200 μg. 2-Keto-1:2:3:4-tetrahydronaphthalene, Ph·[CH<sub>2</sub>]<sub>2</sub>·Br, and NaNH<sub>2</sub> in boiling Et<sub>2</sub>O give 2-keto-1-β-phenylethyl-1:2:3:4-tetrahydronaphthalene, b.p. 210°/6 mm., cyclised (conc. H<sub>2</sub>SO<sub>4</sub> at 0–10°) to 5:6:11:12-tetrahydrochrysene, m.p. 105°. 6-Methoxy-3:4-dihydronaphthalene and BzO<sub>2</sub>H in CH<sub>2</sub>Cl<sub>2</sub> at >10° yield 2-keto-6-methoxy-1:2:3:4-tetrahydronaphthalene, b.p. 135°/0.8 mm. (semicarbazone, m.p. 159°), transformed by (II) and NaNH<sub>2</sub> into its 1-β-*m*-anisylethyl derivative, b.p. 200–205°/0.2 mm., which is cyclised (80% H<sub>2</sub>SO<sub>4</sub> at 70°) to 3:9-dimethoxy-5:6:11:12-tetrahydrochrysene, m.p. 164°. This is demethylated by MgMeI at 180° to the 3:9-(OH)<sub>2</sub>-compound (diacetate, m.p. 187°) and by KOH-EtOH to a phenol which results from a disproportionation of the tetrahydrochrysene ring and is physiologically active only in large doses. The OH-compounds show high oestrogenic activity when a "stilbenoid" double linking occurs between the two aromatic rings in these tri- and tetra-cyclic compounds. Disappearance of the double linking causes great loss of physiological activity.

H. W.

*N*-Alkyl- and *N*-Δ<sup>β</sup>-alkenylidene-aminophenols.—See B., 1942, II, 422.

**Alkyl-oxygen fission in carboxylic esters. II. Derivatives of *p*-methoxybenzhydrol.** M. P. Balfe, M. A. Doughty, J. Kenyon, and R. Poplett (*J.C.S.*, 1942, 605–611; cf. A., 1942, II, 391).—*p*-OMe·C<sub>6</sub>H<sub>4</sub>·CHPh·OH, its esters, and ethers undergo a variety of interconversions when treated with excess of various carboxylic acids or alcohols. Alkyl-O fission of the hydrol and many derivatives is shown by the constitution of the reaction products or by racemisation of an optically active reactant. *dl*-*p*-Methoxybenzhydrol (I), *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O, and C<sub>5</sub>H<sub>5</sub>N (essential) at 55–60° give *dl*-*p*-methoxybenzhydrol *H* phthalate, m.p. 102–103° (decomp.), and thence the (+)-*H* phthalate (II), m.p. 103–103.5°, [α]<sub>D</sub><sup>20</sup> +71.2° in CS<sub>2</sub> [from its cinchonidine salt, m.p. 143–144° (decomp.)]. (II) and NaOH-EtOH (+2% of H<sub>2</sub>O) afford (+)-*p*-methoxybenzhydrol (III), m.p. 58–59°, [α]<sub>D</sub><sup>20</sup> +47.85° in CS<sub>2</sub>; unless the H<sub>2</sub>O content of the NaOH-EtOH is kept low, racemisation occurs. Similar results are obtained with the (–)-*H* phthalate (IV). (III), [α]<sub>D</sub><sup>20</sup> +46.8° in CS<sub>2</sub>, and *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O in C<sub>5</sub>H<sub>5</sub>N (essential) at 50–60° yield (II), [α]<sub>D</sub><sup>20</sup> +38.4° in C<sub>6</sub>H<sub>6</sub> (little racemisation). (III) is completely racemised in H<sub>2</sub>O at 100° (bath) after 30 hr. Racemisation of (II) occurs in EtOH (2 months), AcOH (24 hr.), MeOH (288 hr.), MeNO<sub>2</sub> (19 hr.), or C<sub>6</sub>H<sub>6</sub> (nearly complete after 1656 hr.) at room temp. *dl*-*p*-Methoxybenzhydrol acetate, b.p. 182–183°/4 mm., is prepared from (I) and Ac<sub>2</sub>O or AcCl in C<sub>5</sub>H<sub>5</sub>N, and the benzoate, m.p. 57–58°, from (I) and BzCl-C<sub>5</sub>H<sub>5</sub>N at 50–60°, or from the chloride and aq. NaOBz-COMe<sub>2</sub>. When (I) is distilled at 196–198°/11 mm., a residue (~12%) of *di*-*p*-methoxybenzhydrol ether (V), m.p. 120°, is obtained; this is unaffected by Br-CCl<sub>4</sub>, BzCl-C<sub>5</sub>H<sub>5</sub>N, Ac<sub>2</sub>O, H<sub>2</sub>O, or MeOH, but is converted into (VI) (below) with MeOH-H<sub>2</sub>SO<sub>4</sub>. Distillation of a solution of (IV), [α]<sub>D</sub><sup>20</sup> –2.4° in C<sub>6</sub>H<sub>6</sub>, in dry MeOH during 2.5 hr. gives *dl*-*p*-methoxybenzhydrol Me ether (VI), b.p. 195°/17 mm., m.p. 29° (racemisation indicates alkyl-O fission), also obtained from *di*-*dl*-*p*-methoxybenzhydrol phthalate and MeOH in air (20 days), or by slow distillation of a 5% solution of (I) in MeOH (*o*-methoxybenzhydrol and anisyl-*α*-naphthylcarbinol do not similarly react). Trituration of (III) or (IV) with conc. HCl gives *dl*-*p*-methoxybenzhydrol chloride (VII), also obtained similarly from (V), (VI), or (I) and its *H* phthalate, acetate, or benzoate. (VII) is also obtained from AcCl and (III), (V), or (I) (or acetate), and from (III), SOCl<sub>2</sub>, and C<sub>5</sub>H<sub>5</sub>N. (VII) with cold H<sub>2</sub>O yields (V) [and a little (I)], also obtained from (I), (VII), and a little C<sub>5</sub>H<sub>5</sub>N in Et<sub>2</sub>O. With 3*N*-NaOH or K *H* phthalate in COMe<sub>2</sub>, (VII) affords (I) or its *H* phthalate, respectively. (IV) in aq. NaOH (freshly dissolved; not if kept for 10 min.) or (VII) in COMe<sub>2</sub> with aq. *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>Na (VIII) gives *dl*-*p*-tolyl *p*-methoxybenzhydrol sulphone, m.p. 160°; the reaction with (IV) involves alkyl-O fission, and racemisation of the resulting *p*-methoxybenzhydrol cation. The *H* phthalates of *m*-methoxybenzhydrol, anisyl alcohol, CHMe·CH·CHMe·OH, CHPhMe·OH, CPhMeEt·OH, or octan-β-ol do not react with (VIII); *o*-methoxybenzhydrol *H* phthalate reacts slowly. (–)-Anisylmethylcarbonyl *H* phthalate, [α]<sub>D</sub><sup>20</sup> –18° in EtOH, and (VIII) in aq. NaOH at room temp. yield *dl*-*p*-tolyl *α*-anisylethyl sulphone, m.p. 119–120°, and benzhydrol *H* phthalate gives (when heated) *p*-tolyl benzhydrol sulphone, m.p. 190–191°. (II) and 0.15*N*-NaOH (18 hr.) afford *o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>, (III), [α]<sub>D</sub><sup>20</sup> +3.4° in CS<sub>2</sub>, and *di*-*p*-methoxybenzhydrol phthalate, hydrolysed by aq. NaOH-EtOH to (III), m.p. 55–56° [α]<sub>D</sub><sup>20</sup> +19.0° in CS<sub>2</sub>. (IV) [α]<sub>D</sub><sup>20</sup> –15.7° in C<sub>6</sub>H<sub>6</sub>, and

K *H* phthalate-aq. NaOH at room temp. give (I), and neutral ester, hydrolysed to (I). The *dl*-*H* phthalate and NaOBz-3*N*-NaOH yield *di*-*p*-methoxybenzhydrol phthalate, and BzOH is recovered. (IV), [α]<sub>D</sub><sup>20</sup> –15.7°, and dil. NaOH in presence of (+)-β-octyl *H* phthalate (IX) give an ester, hydrolysed by NaOH-EtOH to (I); (IX) is recovered. (II) and (IX) also lead to (I). Benzhydrol, new m.p. 157–158°, phenylmethylcarbonyl, and γ-phenyl-*α*-methylallyl *H* phthalates show little change with aq. NaOH (1 mol.) at room temp., but when heated give the alcohols. Some aspects of the mechanism of the formation of the neutral ester remain obscure.

A. T. P.

**Restricted rotation in arylolefines. IV. Preparation and resolution of β-chloro-β-3-chloro-6-methoxy-2:4-dimethylphenyl-*α*-methylacrylic and the corresponding acrylic acid.** R. Adams and W. J. Gross. **V. β-Bromo-β-2-alkoxy-1-naphthyl-*α*-alkylacrylic acids.** R. Adams, L. O. Binder, and F. C. McGrew. **VI. Substituted β-2:7-dimethoxy-1-naphthyl-*α*-methylacrylic acids.** R. Adams, M. W. Miller, F. C. McGrew, and A. W. Anderson (*J. Amer. Chem. Soc.*, 1942, 64, 1786–1790, 1791–1794, 1795–1801; cf. A., 1942, II, 93).—IV. *o*-Me has a greater steric effect than has *o*-OMe. 1:3:5-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>·OMe, (EtCO)<sub>2</sub>O, and AlCl<sub>3</sub> in boiling CS<sub>2</sub> give 2-methoxy- (I) (75%), b.p. 120–122°/2 mm., and some 2-hydroxy-4:6-dimethylpropionophenone, m.p. 78° [converted into (I) by Me<sub>2</sub>SO<sub>4</sub>-aq. NaOH at 100°]. Et<sub>2</sub>O-MgEtBr and then CO<sub>2</sub> at 0°/2–3 atm. and later room temp. convert (I) into *α*-2-methoxy-4:6-dimethylbenzoylpropionic acid (30%), m.p. 88–89°, which with PCl<sub>5</sub>-POCl<sub>3</sub> at 70° gives a mixture of small amounts of β-chloro-β-2-methoxy-4:6-dimethyl-, m.p. 163–164°, and β-3-chloro-6-methoxy-2:4-dimethyl- (II), m.p. 178–179°, phenyl-*α*-methylacrylic acid. 3:5:4:1-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>Cl·OH and Me<sub>2</sub>SO<sub>4</sub> in boiling aq. NaOH give 2-chloro-*m*-5-xylene *Me* ether (80%), b.p. 94–96°/6 mm., which yields, as above, 3-chloro-6-methoxy-2:4-dimethylpropionophenone (55%), m.p. 66.5–67.5°, *α*-3-chloro-6-methoxy-2:4-dimethylbenzoylpropionic acid (50%), m.p. 118°, and (II) (50%). With quinine in warm COMe<sub>2</sub>, (II) gives the salt, [α]<sub>D</sub><sup>20</sup> –30.0° in C<sub>6</sub>H<sub>6</sub>, and thence the *d*-acid, m.p. 177°, [α]<sub>D</sub><sup>20</sup> +22.5° in Bu<sup>o</sup>OH, having a half-life period 173 min. in Bu<sup>o</sup>OH at 44° and very short at the b.p. With Ac<sub>2</sub>O-AlCl<sub>3</sub>-CS<sub>2</sub>, 3:5:4:1-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>Cl·OMe gives 3-chloro-6-methoxy-2:4-dimethylacetophenone (70%), m.p. 76–77°, b.p. 134–136°/3 mm., and thence, as above, β-keto-β-3-chloro-6-methoxy-2:4-dimethylphenylpropionic acid (45%), m.p. 113°, *dl*-, m.p. 181–182°, and *d*-β-chloro-β-3-chloro-6-methoxy-2:4-dimethylphenylacrylic acid, m.p. 180°, [α]<sub>D</sub><sup>20</sup> +12.5° in Bu<sup>o</sup>OH, half-life period 9 min. in Bu<sup>o</sup>OH at 20° (quinine salt, [α]<sub>D</sub><sup>20</sup> –25.0° in C<sub>6</sub>H<sub>6</sub>). Similarly are prepared 2-chloro-*m*-5-xylene *Et* ether, 3-chloro-6-ethoxy-2:4-dimethylpropion-, m.p. 53–54°, b.p. 155–156°/7 mm., and *aceto*-phenone, m.p. 74°, b.p. 145–147°/7 mm., *α*-3-chloro-6-ethoxy-2:4-dimethylbenzoylpropionic, m.p. 115.5–116.5°, β-keto-β-3-chloro-6-ethoxy-2:4-dimethylphenylpropionic, m.p. 103–104°, β-chloro-β-3-chloro-6-ethoxy-2:4-dimethylphenyl-*α*-methylacrylic, m.p. 141–142°, and *acrylic* acid, m.p. 176–177°. These acrylic acids do not give cryst. alkaloidal salts.

V. The smaller steric effect of the *peri*-CH of a C<sub>10</sub>H<sub>8</sub> nucleus compared with an *o*-Me is confirmed. 2:1-OMe·C<sub>10</sub>H<sub>6</sub>·CHO, EtCO<sub>2</sub>Na, and (EtCO)<sub>2</sub>O at 170° give *trans*-β-2-methoxy-1-naphthyl-*α*-methylacrylic acid (III) (62%) (here and below *trans* and *cis* refer to the CO<sub>2</sub>H and aryl nucleus), m.p. 155–156°, converted by Br-CHCl<sub>3</sub> in the dark into the β-*Br*-acid (IV) (38%), m.p. 208° (oxidised by KMnO<sub>4</sub> to 2:1-OMe·C<sub>10</sub>H<sub>6</sub>·CO<sub>2</sub>H; hence structure). 2:1-OH·C<sub>10</sub>H<sub>6</sub>·CHO, EtCO<sub>2</sub>Na, and (EtCO)<sub>2</sub>O at 170° give 3-methylnaphthyl-1':2'-5:6-2-pyrone ["2-methyl-4:3-β-naphthopyrone"] (60%), m.p. 156°, which with aq. KOH at 90° and then warm aq. Me<sub>2</sub>SO<sub>4</sub>-alkali gives (III) or occasionally its *cis*-isomeride, m.p. 167°, converted by Br-CHCl<sub>3</sub> into a little (IV) and non-acidic material, m.p. 93°. 2:1-OEt·C<sub>10</sub>H<sub>6</sub>·CHO gives similarly β-2-ethoxy-1-naphthyl- (43%), m.p. 130°, and β-bromo-β-2-ethoxy-1-naphthyl- (V) (29%), m.p. 172°, *α*-methylacrylic acid. In boiling 48% aq. HBr-AcOH, (IV) gives 4-bromo-3-methylnaphthyl-1':2'-5:6-2-pyrone (56%), m.p. 186°, which by hydrolysis and subsequent methylation yields the *cis*-isomeride (VI), m.p. 187°, of (IV). Perkin reactions using Pr<sup>o</sup>CO<sub>2</sub>K and (Pr<sup>o</sup>CO)<sub>2</sub>O and subsequent treatment as above give *trans*- (VII) (40%), m.p. 110°, and *cis*-β-2-methoxy-1-naphthyl-*α*-ethylacrylic acid (VIII), m.p. 120°, and 3-ethylnaphthyl-1':2'-5:6-2-pyrone (IX), m.p. 111°. With Br-CHCl<sub>3</sub>, (VII) or (VIII) gives the 4-*Br*-derivative, m.p. 137°, of (IX) and thence (boiling KOH-EtOH; then aq. KOH-Me<sub>2</sub>SO<sub>4</sub>) β-bromo-β-2-methoxy-1-naphthyl-*α*-ethylacrylic acid (X), m.p. 138°. (IV), (VI), (V), and (X) give single cryst. salts, which do not mutarotate and regenerate the *dl*-acids.

VI. 2:7-C<sub>10</sub>H<sub>6</sub>(OH)<sub>2</sub>, Zn(CN)<sub>2</sub>, and HCl in Et<sub>2</sub>O give 2:7:1-(OH)<sub>2</sub>C<sub>10</sub>H<sub>5</sub>·CHO (XI), m.p. 159–160°, converted by Me<sub>2</sub>SO<sub>4</sub> in 25% aq. KOH into 2-hydroxy-7-methoxy-1-naphthaldehyde (XII) (60%), m.p. 128–129°, which with EtCO<sub>2</sub>K-(EtCO)<sub>2</sub>O at 175–180° gives 7'-methoxy-3-methylnaphthyl-1':2'-5:6-2-pyrone (XIII), m.p. 186.5–187.5°. The Perkin reaction with (XI) yields the 7'-propionoxy-, m.p. 161–162°, and thence the 7'-OH-pyrone, m.p. 263–266° (block), which affords (XIII). With HNO<sub>3</sub> (*d* 1.42) in AcOH, (XIII) gives its 8'-NO<sub>2</sub>-, m.p. 276–278°, and with Br-CHCl<sub>3</sub> at 0° its 8'-*Br*-derivative (XIV), m.p. 218–219°. With Br-CCl<sub>4</sub>, (XII) gives 8-bromo-2-hydroxy-7-methoxy-1-naphthaldehyde (57%), m.p. 97–99°, and thence (Perkin) (XIV). Hot KOH-EtOH, then Me<sub>2</sub>SO<sub>4</sub>

in 5% aq. KOH at room temp., and finally boiling 20% aq. KOH convert (XIII) and (XIV) into  $\beta$ -2 : 7-dimethoxy- (XV), form, m.p. 158—159°, and  $\beta$ -bromo- $\beta$ -2 : 7-dimethoxy-1-naphthyl- $\alpha$ -methylacrylic acid (XVI), form, m.p. 166° (decomp.) (quinine salt, m.p. 98—99°, does not mutarotate). Methylation of (XI) also affords 2 : 7-dimethoxy-1-naphthaldehyde (XVII) (69%), m.p. 99—100° [semicarbazone, m.p. 247° (block)], which yields (Perkin) a form (XVIII), m.p. 153°, of (XV), which is converted thereto by illumination in EtOH. Br and (XVIII) in  $\text{CHCl}_3$  give a form, m.p. 190°, of (XVI); this gives quinine, m.p. 183—184°,  $[\alpha]_D^{25} -77.4^\circ$  in EtOH, and brucine salts, m.p. 208—210° (decomp.),  $[\alpha]_D^{25} -52.5^\circ$  in EtOAc, which do not mutarotate and regenerate the *dl*-acid; it resists further bromination. With  $\text{HNO}_3$  (*d* 1.2) in AcOH, (XVIII) gives its 8- $\text{NO}_2$ -derivative, m.p. 197—198°, irresolvable by way of its quinine salt, m.p. 156°,  $[\alpha]_D^{25} -34.3^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . 2 : 7- $\text{C}_{10}\text{H}_6(\text{OMe})_2$  and Br in  $\text{CHCl}_3$  give 1-bromo-2 : 7-dimethoxynaphthalene, m.p. 88—89°, converted by LiBu in  $\text{Et}_2\text{O}$  and then solid  $\text{CO}_2$  into 2 : 7-dimethoxy-1-naphthoic acid, m.p. 112—113°, which is also obtained from (XVII) (proof of structure) in poor yield by  $\text{KMnO}_4$  in aq.  $\text{Na}_2\text{CO}_3$  at room temp. With  $\text{HNO}_3$  (*d* 1.42) in AcOH, (XVII) gives 8-nitro-2 : 7-dimethoxy-1-naphthaldehyde, m.p. 190°, which is also obtained from 2 : 7 : 1-(OMe) $_2\text{C}_{10}\text{H}_6\cdot\text{NO}_2$  by  $\text{Zn}(\text{CN})_2\text{--AlCl}_3\text{--HCl--C}_6\text{H}_6$  and does not undergo the Perkin reaction. (XVII) gives an oxime, m.p. 181—182°, and thence (boiling  $\text{Ac}_2\text{O}$ ) 2 : 7-dimethoxy-1-naphthonitrile, m.p. 129°, which resists hydrolysis. M.p. (all parts) arc corr. R. S. C.

**Influence of substrate structure on kinetics of carboxypolypeptidase action.** M. Bergmann and J. S. Fruton (*J. Biol. Chem.*, 1942, 145, 247—252).—See A., 1943, III, 57. Carbobenzyloxy-*l*-alanyl chloride and *l*-phenylalanine Et ester in  $\text{Et}_2\text{O}$  afford carbobenzyloxy-*l*-alanyl-*l*-phenylalanine Et ester, m.p. 97—98°, hydrolysed to carbobenzyloxy-*l*-alanyl-*l*-phenylalanine, m.p. 56—58°. Carbobenzyloxy-*l*-alanyl-*l*-tyrosine, m.p. 149—150°, and its Et ester, m.p. 138—139°, are obtained similarly. H. W.

**Multiple specificity of chymotrypsin.** J. S. Fruton and M. Bergmann (*J. Biol. Chem.*, 1942, 145, 253—265).—See A., 1943, III, 57. Carbobenzyloxyglycyl-*l*-tyrosine Et ester is converted by  $\text{NH}_2$  in MeOH into carbobenzyloxyglycyl-*l*-tyrosinamide, m.p. 170°, hydrogenated in presence of MeOH and AcOH to glycyl-*l*-tyrosinamide acetate,  $[\alpha]_D^{22} +28.0^\circ$  in  $\text{H}_2\text{O}$ . Carbobenzyloxyglycyl-*l*-phenylalaninamide, m.p. 130°, and glycyl-*l*-phenylalaninamide acetate,  $[\alpha]_D^{25} +28.8^\circ$  in  $\text{H}_2\text{O}$ , are obtained similarly. Analogous series of changes yield the following: carbobenzyloxy-*l*-phenylalaninamide, m.p. 167°, and *l*-phenylalaninamide acetate, m.p. 119—120°; *l*-tyrosylglycinamide acetate; carbobenzyloxy-*l*-phenylalanylglycinamide, m.p. 134°, and *l*-phenylalanylglycinamide acetate; carbobenzyloxy-*l*-tyrosyl-*l*-tyrosinamide, m.p. 187—189°, and *l*-tyrosyl-*l*-tyrosinamide acetate; N-carbenzyloxy-O-acetyl-*l*-tyrosyl-*l*-phenylalanine Et ester, m.p. 170°, and carbobenzyloxy-*l*-tyrosyl-*l*-phenylalaninamide, m.p. 220°; carbobenzyloxy-*l*-phenylalanyl-*l*-tyrosine Et ester, m.p. 162°, carbobenzyloxy-*l*-phenylalanyl-*l*-tyrosinamide, m.p. 221°, and *l*-phenylalanyl-*l*-tyrosinamide, m.p. 180°; carbobenzyloxy-*l*-phenylalanyl-*l*-phenylalanine Et ester, m.p. 140°, carbobenzyloxy-*l*-phenylalanyl-*l*-phenylalaninamide, m.p. 230°, and *l*-phenylalanyl-*l*-phenylalaninamide, m.p. 138°; carbobenzyloxyglycylglycinamide, m.p. 179—181°, and glycylglycinamide acetate. Carbobenzyloxyphenylalanylglycine Et ester is hydrolysed to carbobenzyloxy-*l*-phenylalanylglycine, m.p. 152°, and converted by  $\text{NH}_3$  in MeOH at 0° into 5-benzylhydantoin-3-acetamide, m.p. 216—218° (corresponding acid, m.p. 185—186°). H. W.

**Halogenation of unsaturated compounds.**—See A., 1943, II, 2.

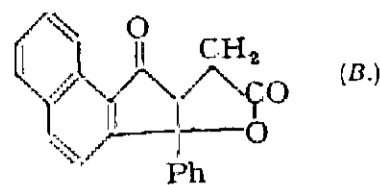
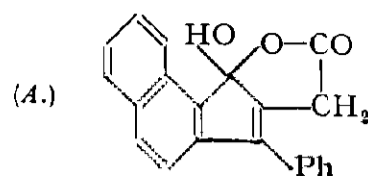
**Identification of amides through the mercury derivatives.** J. W. Williams, W. T. Rainey, jun., and R. S. Leopold (*J. Amer. Chem. Soc.*, 1942, 64, 1738—1739).—Amides and  $\text{HgO}$  at the m.p. or, in some cases, in boiling 95% EtOH give derivatives,  $\text{Hg}(\text{NHAcyl})_2$ . Compounds in which Acyl = Ac, m.p. 196—197°, EtCO, m.p. 201°, PrCO, m.p. 222—224°, Bz, m.p. 222°, m-, m.p. 245°, and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}$ , m.p. 258°, o-, m.p. 242°, m-, m.p. 235°, and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}$ , m.p. 266°, o-, m.p. 196°, m-, m.p. 200°, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}$ , m.p. 260°, o-, m.p. 241°, and *p*-anisoyl, m.p. 222°, and o- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}$ , m.p. 190°, are described. R. S. C.

**Solvent effects in association equilibria.**—See A., 1943, I, 15.

**Dialkylaminoalkyl fluorene-9-carboxylates [antispasmodic agents].**—See B., 1942, III, 277.

**Condensation of aromatic ketones with ethyl succinate.** C. L. Hewett (*J.C.S.*, 1942, 585—587).— $\text{CHPh}\cdot\text{CPh}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (Stobbe *et al.*, A., 1899, i, 902) is reduced by Na-Hg in aq. NaOH to two isomeric  $\gamma\delta$ -diphenylbutane- $\alpha\beta$ -dicarboxylic acids, m.p. 188—189° and 138° (slightly impure), both of which with conc.  $\text{H}_2\text{SO}_4$  (1 min. at 100°) give mixtures of two stereoisomeric 3 : 10-diketo-3 : 4 : 9 : 10 : 11 : 12-hexahydro-1 : 2-benzanthracenes, m.p. 210—211° (probably *trans*-) and 132—133° (*cis*-, converted into *trans*- during an attempted Clemmensen reduction).  $(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$  (I), 2- $\text{C}_{10}\text{H}_7\cdot\text{COPh}$ , and NaOEt in  $\text{Et}_2\text{O--EtOH}$  afford  $\gamma$ -phenyl- $\gamma$ -naphthylitaconic acid, m.p. 173.5—174.5° (*Me* $_2$  ester, m.p. 94—95°), reduced

(Na-Hg) to  $\alpha$ -(phenylnaphthylmethyl)succinic acid (II), m.p. 130—131°, and cyclised by conc.  $\text{H}_2\text{SO}_4$  at room temp. to the lactone,  $\text{C}_{21}\text{H}_{14}\text{O}_3$  (A or B), m.p. 166.5—167.5°. The anhydride (prep. by



$\text{AcCl}$  of (II) with  $\text{AlCl}_3$  in  $\text{PhNO}_2$  at 0° gives 4-keto-1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-phenanthroic acid, m.p. 243—245° (sinters at 240°). (I) and 6-benzoyl-1 : 2 : 3 : 4-tetrahydronaphthalene give two  $\gamma$ -phenyl- $\gamma$ -6-tetrahydronaphthylitaconic acids, m.p. 183—185° (III) and 188—189°, only slightly affected by Na-Hg. With conc.  $\text{H}_2\text{SO}_4$  at room temp. (1 min.) (III) affords (probably) 3-phenyl-5 : 6-tetramethyleneindone-2-acetic acid, m.p. 165—166°. A. T. P.

**Production of benzaldehyde by oxidation of toluene.**—See B., 1942, II, 417.

**3- $\beta$ -D-Glucosidoprotocatechualdehyde.**—See A., 1943, II, 4.

**Chromatography of *cis*- and *trans*-benzoin- and -anisoin-oximes with application of the brush method.** L. Zechmeister, W. H. McNealy, and G. Solyom (*J. Amer. Chem. Soc.*, 1942, 64, 1922—1924).—*cis*- and *trans*-Benzoin- and -anisoin-oximes are separated by adsorption on Neutral Filtrol (+ a filter aid), extruding the column, and painting a streak by aq.  $\text{CuSO}_4\text{--NH}_3$  down the column. The *trans*- and *cis*-oxime zones give green and brown colours, respectively. Isomerisation on the column is <5%. 1—2% of one form can be detected in the other. R. S. C.

**Indeno-2' : 3' : 2 : 3-benzanthrone.** G. Swain and A. R. Todd (*J.C.S.*, 1942, 626—628).—Methyleneanthrone (I) and indene in boiling  $\text{PhNO}_2$  give indeno- (II), m.p. 218—219°, and a dihydroindeno-2' : 3' : 2 : 3-benzanthrone (III), m.p. 252—253°; in  $\text{C}_6\text{H}_6$  or xylene only (III) results. Dehydrogenation of (III) to (II) is effected by Pd-C at 270—310° (inert atm.) or (partly) by boiling  $\text{PhNO}_2$ . (II) or (III) and  $\text{SeO}_2\text{--H}_2\text{O}$  at 230° afford 1'-ketoideno-2' : 3' : 2 : 3-benzanthrone (IV), m.p. 336—338°. (I), Et cinnamate, and  $\text{PhNO}_2$  give Et 3-phenylbenzanthrone-2-carboxylate, m.p. 155—156°, with a little of (probably) a dimorph, m.p. 190—210°, both hydrolysed by aq. KOH-EtOH to the 2-carboxylic acid (V), m.p. 284—286°, converted by quinoline-Cu-bronze into 3-phenylbenzanthrone, m.p. 182—183°. (V) and  $\text{H}_2\text{SO}_4$  at 100° (bath) give (IV). (II) and (IV) show tumour-inhibitory properties of a moderate order. A. T. P.

**Synthesis of emodin and of fumigatin.** T. Posternak, J. P. Jacob, and H. Ruelius (*Arch. Sci. phys. nat.*, 1941, [v], 23, Suppl., 223—225).—3 : 5 : 1-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{Me}$  and 2 : 4 : 5 : 1-OMe- $\text{C}_6\text{H}_2\text{MeBr}\cdot\text{COCl}$  afford (Friedel-Crafts) Me 5'-bromo-2 : 4 : 2'-trimethoxy-4'-methylbenzophenone-6-carboxylate; the free acid is cyclised and partly demethylated by oleum to 1-bromoemodin Me $_2$  ether, converted (methods: Jacobson *et al.*, A., 1924, i, 752) into emodin [4 : 5 : 7-trihydroxy-2-methylantraquinone]. 3 : 5 : 4 : 1-(OH) $_2\text{C}_6\text{H}_2(\text{OMe})\cdot\text{CHO}$  is reduced ( $\text{H}_2$ , Pd-black, AcOH) to 3 : 5 : 1 : 4-(OH) $_2\text{C}_6\text{H}_2\text{Me}\cdot\text{OMe}$ , the 2- $\text{NO}$ -derivative (prep. by  $\text{C}_6\text{H}_{11}\cdot\text{O}\cdot\text{NO}$ ) of which is reduced to the 2- $\text{NH}_2$ -compound. This is oxidised ( $\text{FeCl}_3$ ) to fumigatin [3-hydroxy-4-methoxy-2 : 5-toluquinone]. C. S.

## IV.—STEROLS AND STEROID SAPOGENINS.

**H. Wieland's work on sterols.** E. Dane (*Naturwiss.*, 1942, 30, 333—342).—A review. F. O. H.

**Bio-reduction of sterols.**—See A., 1942, III, 915.

**Seeds of *Alangium lamarckii*.** I. A. Lakshminarasimhaiah, B. L. Manjunath, and B. S. Nagaraj (*J. Mysore Univ.*, 1942, 3, B, 113—116).—The light petroleum (b.p. 40—70°) extract of the seeds contains a sterol ("alangol"),  $\text{C}_{30}\text{H}_{48}$  (or 50) $\text{O}_2$ , m.p. 302—307° (slight decomp.), having 4 double linkings and 3 active H [mono-( $\text{Ac}_2\text{O}$ ), m.p. 262—265°, and di-acetate (HCl in AcOH), m.p. 330—334° (decomp.)]. A. Li.

**Colour reaction between ergosterol and methyldichloroarsine.** P. M. Baranger and J. M. Mercier (*Biochem. J.*, 1942, 36, 703—705).— $\text{AsMeCl}_2$  gives a golden-yellow coloration with a freshly prepared solution of ergosterol in  $\text{CHCl}_3$ ; the max. extinction coeff.  $\propto [\text{AsMeCl}_2]$ . The substances used must be pure and dry. H. G. R.

**7-Dehydrocampesterol, a new provitamin-D.** W. L. Ruigh (*J. Amer. Chem. Soc.*, 1942, 64, 1900—1902).—Campesterol acetate and  $\text{CrO}_3\text{--AcOH}$  give 7-ketocampesterol acetate, m.p. 177—178°,  $[\alpha]_D^{24} -88.6^\circ$  in  $\text{CHCl}_3$ , reduced by  $\text{Al}(\text{OPr}^i)_3\text{--Pr}^i\text{OH}$  to 7( $\alpha$ )-hydroxycampesterol, the dibenzoate, m.p. 176.5—177.5°,  $[\alpha]_D^{25} +96.6^\circ$  in  $\text{CHCl}_3$ , of which with NaOMe-MeOH at room temp. yields 7( $\alpha$ )-benzoyloxycampesterol, m.p. 143—145° (sinters at 126—130°),  $[\alpha]_D^{26} +115.0^\circ$  in  $\text{CHCl}_3$ . In boiling NPhMe $_2$  this gives, by way of the digitonide and after benzylation, 7-dehydrocampesterol benzoate,

m.p. 156—157° (clear at 164°; vac.), and thence (boiling 5% KOH-MeOH) 7-dehydrocampesterol (I), m.p. 164—165° (vac.),  $[\alpha]_D^{25}$  -109.0° in CHCl<sub>3</sub> [absorption max. at 272 and 282 mμ. ( $\epsilon$  10,600)]. By comparison with ergosterol, irradiation of (I) gives a product the antirachitic potency of which is 4,100,000 i.u. per g.

R. S. C.

**Minor sterols of yeast. X. Relationships between lanosterol and cryptosterol.** H. Wieland and W. Benend [with, in part, E. Joust] (*Z. physiol. Chem.*, 1942, 274, 215—222).—Lanosterol (I) and cryptosterol (II) differ from one another solely in the position of the difficultly reactive double linking and are otherwise identical in structure and configuration. Ozonisation of (I) or (II) gives COMe<sub>2</sub> identified as the 2:4-dinitrophenylhydrazone, m.p. 128°, in 40% and >50% yield whereas dihydro-lanosterol (III) and -cryptosterol (IV) yield only CH<sub>2</sub>O in small amount. The active double linking in (I) and (II) is therefore in the group >C:CMe<sub>2</sub>. Cryptosteryl acetate is converted by successive treatments with OsO<sub>4</sub> in Et<sub>2</sub>O and Na<sub>2</sub>SO<sub>3</sub> into cryptostenetriol acetate, m.p. 177—179°, hydrolysed to the triol (V), m.p. 178—180°,  $[\alpha]_D^{20}$  +50.50° in CHCl<sub>3</sub>, also obtained by treating (II) with OsO<sub>4</sub> in Et<sub>2</sub>O-C<sub>5</sub>H<sub>5</sub>N and the product with alkaline mannitol. (V) and Pb(OAc)<sub>4</sub> in C<sub>6</sub>H<sub>6</sub> give COMe<sub>2</sub> in 80% yield but no CH<sub>2</sub>O. Dihydrocryptosteryl acetate (VI), (III), (VII) (below), and  $\alpha$ -cholesterol are resistant to OsO<sub>4</sub> whereas dihydrozymosterol gives an almost quant. yield of ester. (IV) is converted by HCl in boiling CHCl<sub>3</sub> into isodihydrocryptosterol (VII), m.p. 135—136°,  $[\alpha]_D^{20}$  +40.5° in CHCl<sub>3</sub>, which could not be hydrogenated (PtO<sub>2</sub> in AcOH). (VI) is similarly isomerised to isodihydrocryptosteryl acetate, m.p. 130°,  $[\alpha]_D^{20}$  +44.5° in CHCl<sub>3</sub>. The corresponding benzoate has m.p. 197—198°,  $[\alpha]_D^{20}$  +61° in CHCl<sub>3</sub>. The double linking of (VI) does not absorb Br. isoDihydrolanosterol, m.p. 135—136°,  $[\alpha]_D^{20}$  +38° (acetate, m.p. 129—130°,  $[\alpha]_D^{20}$  +43.6°, benzoate, m.p. 197—198°,  $[\alpha]_D^{20}$  +60.3°), is prepared. H. W.

**Action of lead tetra-acetate on sterol derivatives.** A. Windaus and U. Riemann (*Z. physiol. Chem.*, 1942, 274, 206—214).—Ergosteryl acetate is converted by Pb(OAc)<sub>4</sub> in CHCl<sub>3</sub>-AcOH at 20° into  $\Delta^7:22$ -ergostadiene-3:5:6-triol diacetate, m.p. 181—182°, hydrolysed (KOH-EtOH) to the triol, m.p. 241—242°. Under similar conditions 7-dehydrocholesteryl acetate affords  $\Delta^7$ -cholestene-3:5:6-triol diacetate, m.p. 195°, hydrolysed to the triol, m.p. 238—239°. Vitamin-D<sub>2</sub> 3:5-dinitrobenzoate and Pb(OAc)<sub>4</sub> give 5:6-dihydroxydihydrovitamin-D<sub>2</sub> 3:5-dinitrobenzoate, m.p. 174°, hydrolysed (KOH-MeOH) to 5:6-dihydroxydihydrovitamin-D<sub>2</sub> (I), m.p. 157°,  $[\alpha]_D^{20}$  +50° in CHCl<sub>3</sub>, in which the absence of a conjugated double linking is established spectroscopically. The structure of (I) is confirmed by oxidation [Pb(OAc)<sub>4</sub>] to the aldehyde, new m.p. 59°, of Heilbron *et al.* (A., 1936, 1105). Hydrogenation (Pt-sponge in EtOAc) of (I) gives a mixture of products from which (?) dihydroxytetrahydrovitamin-D<sub>2</sub> (II), m.p. 199—202°,  $[\alpha]_D$  +60° in CHCl<sub>3</sub> (3:5-dinitrobenzoate, m.p. 191°), is isolable; it appears to contain the double linking between C<sub>7</sub> and C<sub>8</sub> intact since it is oxidised [Pb(OAc)<sub>4</sub> in CHCl<sub>3</sub>-AcOH] to an aldehyde (semicarbazone, C<sub>22</sub>H<sub>39</sub>ON<sub>3</sub>, m.p. 242°). Further hydrogenation (Pt-sponge in AcOH) of (II) yields dihydroxyhexahydrovitamin-D<sub>2</sub>, m.p. 103°,  $[\alpha]_D$  +24.8° in CHCl<sub>3</sub> (dibenzoate, m.p. 211°). Vitamin-D<sub>3</sub> 3:5-dinitrobenzoate is converted by Pb(OAc)<sub>4</sub> into a non-cryst. ester, hydrolysed to dihydroxydihydrovitamin-D<sub>3</sub>, m.p. 156°, which with AcOH-CHCl<sub>3</sub>-conc. H<sub>2</sub>SO<sub>4</sub> gives the same colour reaction as (I). H. W.

**Autoxidation of sterols in colloidal aqueous solution. III. Quantitative studies on cholesterol. IV. Influence of esterification and of constitutional factors.** S. Bergström and O. Wintersteiner (*J. Biol. Chem.*, 1942, 145, 309—326, 327—333).—III. 7-Ketocholesterol (I) has been determined by ultra-violet absorption measurements and the 7-hydroxycholesterols (II) by the Lifschütz reagent in the products of the autoxidation of aq. cholesterol sols. The rate of reaction is primarily dependent on temp. whilst concn., pH, O<sub>2</sub> pressure, and the nature of the detergent exert comparatively little influence. At 85° the reaction invariably comes to a standstill after a few hr. with ~40% of (I) and 20% of (II) formed. Autoxidation is limited to these levels by accumulation of the reaction products. Both types of these participate in bringing about this inhibition but each of them more specifically hinders the formation of its own kind. Small quantities of CN' completely stop the autoxidation. With still smaller concns. of CN' the reaction is merely delayed and then proceeds until normal levels are reached. The CN'-inhibited system can be reactivated by Cu<sup>++</sup>. Fe<sup>++</sup> and Zn<sup>++</sup> moderately accelerate the spontaneous reaction but do not effect a greater conversion. Mn<sup>++</sup> causes a very marked inhibition whilst PhOH, salicylaldehyde, and hæmin completely prevent the reaction. Whenever inhibition occurs the formation of both (I) and (II) is retarded or entirely suppressed. A reaction mechanism involving the intermediate formation of a cholesterol 7-peroxide is discussed.

IV. Study of the course of the autoxidation of cholesteryl acetate, palmitate, and oleate in aq. colloidal solution at 85° shows that esterification greatly diminishes the susceptibility to attack by O<sub>2</sub>. Compounds of the cholesterol type [stigmasterol, campesterol, fucosterol, and Me 3( $\beta$ )-hydroxy- $\Delta^5$ -cholesterol] are oxidised in the typical manner to 7-ketones and chromogens. The reaction curves resemble

those obtained with cholesterol except that the final levels of ketone and chromogens are lower in all cases. *allo*Cholesterol and  $\Delta^5$ -cholestene-3:4-diol do not appear to be autoxidised under these conditions.  $\alpha$ -Spinasterol does not yield any Lifschütz-positive products but the absorption spectra indicate that two ketones with max. at 245 and 253 mμ. have been formed. H. W.

**Sterol ketones.**—See B., 1942, III, 277.

**Sterols. CXLIX. Hypoiodite oxidation of pregnan- and pregnenolones.** R. E. Marker and R. B. Wagner (*J. Amer. Chem. Soc.*, 1942, 64, 1842—1843).—3( $\beta$ )-Acetoxy-pregnan-, - $\Delta^{16}$ -pregnen-, - $\Delta^5$ -pregnen-, and - $\Delta^5:16$ -pregnadien-20-one with I-KI-KOH-H<sub>2</sub>O-dioxan first at room temp. and then at 80° (then aq. KOH at 100°) give 3( $\beta$ )-hydroxy- $\alpha$ -tiocholanolic (I), m.p. 224—226° (Me ester, m.p. 128°), - $\Delta^{16}$ - $\alpha$ -tiocholanolic (II), m.p. 254—256° (Me ester, m.p. 150—152°), - $\Delta^5$ - $\alpha$ -tiocholanolic, m.p. 273—274°, and - $\Delta^5:16$ - $\alpha$ -tiocholadienolic acid, m.p. 255—257°, respectively. H<sub>2</sub>-PtO<sub>2</sub> reduces (II) in AcOH at 3 atm. to (I). R. S. C.

**Sterols. CL. Sapogenins. LXIII. Position of the hydroxyl groups in digitogenin.** R. E. Marker, D. L. Turner, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1942, 64, 1843—1847).—The second OH of digitogenin (I) is not at C<sub>6</sub> and may be at C<sub>15</sub>. Cholestane-3:6-diol and CrO<sub>3</sub> in AcOH at 70° give 6-ketocholestane-2:3-diacid (II), m.p. 228—230° (gas), which with Zn-Hg-conc. HCl-EtOH and then KOH-EtOH gives cholestane-2:3-diacid. H<sub>2</sub>-PtO<sub>2</sub> in AcOH at 40 lb. reduces (II) to a lactone-acid, C<sub>27</sub>H<sub>44</sub>O<sub>4</sub>, m.p. 188—190°, but digitogenic or digitonic acid in MeOH to a dicarboxylic acid, C<sub>27</sub>H<sub>42</sub>O<sub>7</sub>, m.p. 285—290° (decomp.). KHSO<sub>4</sub> at 200—210°/high vac. converts chlorogenin into 3:5-dehydrodeoxytigogenin, but has no effect on (I). 6-Ketotigogenone (prep. from diosgenin by CrO<sub>3</sub>; =chlorogenone) and CrO<sub>3</sub>-AcOH at <30° or, better, Kiliani's acid give chlorogenonic acid, m.p. (anhyd.) 232—234° or +AcOH. Digitogenin triacetate and CrO<sub>3</sub>-AcOH at 100° give digitogenin lactone triacetate and CO<sub>2</sub>H-CH<sub>2</sub>-CHMe-CO<sub>2</sub>H. Boiling HCl-EtOH has no effect on (I), which thus has the *iso*-configuration. (I) is unaffected by Zn-Hg-HCl-EtOH or Ac<sub>2</sub>O at 200°, whereas other sapogenins give H<sub>4</sub>- and  $\psi$ -compounds, respectively. R. S. C.

## V.—TERPENES AND TRITERPENOID SAPOGENINS.

**Synthetic menthols.** W. E. Huggett (*Quart. J. Pharm.*, 1942, 15, 218—227).—Mainly a review of the 12 menthols dealing with physical consts., physiological, pharmacodynamic, and pharmacological properties. When 1 g. of H<sub>3</sub>PO<sub>4</sub> (*d* 1.75) is mixed with 4.25 g. of synthetic menthol previously dried by boiling, a mixture which has a well-defined setting point and m.p. is obtained. A setting point of 60° or m.p. of 61° is obtained when the *dl*-menthol is free from isomerides; lower vals. indicate their presence. The method is applicable to optically active, inactive, or partly active material, and when the impurity is isomenthol an estimate of the amount to within 1% for any mixture containing 0—40% can easily be obtained. The composition of any mixture of isomerides is not readily determined. *dl*-Menthol has m.p. 38° and 27—28° (2 cryst. forms). J. N. A.

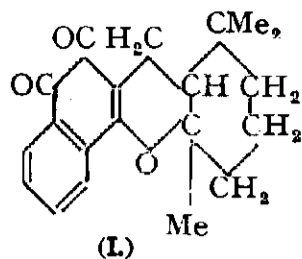
**Separation of diastereoisomerides by selective adsorption on optically inactive material.** (Miss) M. M. Jamison and E. E. Turner (*J.C.S.*, 1942, 611—612).—*l*-Menthyl *d*- and *l*-mandelates are adsorbed selectively on Al<sub>2</sub>O<sub>3</sub>. F. R. S.

**Constituents of the volatile oil of catnip. II. Neutral components. Nepetalic anhydride.** S. M. McElvain, P. M. Walters, and R. D. Bright (*J. Amer. Chem. Soc.*, 1942, 64, 1828—1831; cf. A., 1942, II, 124).—The part (10%) of the oil insol. in 10% NaOH at 60°/15 min. is resolved by fractionation into  $\beta$ -caryophyllene (I) (14%), nepetalactone (II) (42%), an ether, C<sub>14</sub>H<sub>24</sub>O (3%), b.p. 85—87°/0.03 mm., an ester, (C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>)<sub>x</sub> (*x* = ? 2) (2%), b.p. 115—117°/1 mm., and nepetalic anhydride (III), (Me·C<sub>5</sub>H<sub>7</sub>· $\begin{smallmatrix} \text{CO-O} \\ \text{CHMe} \end{smallmatrix}$ ·CH)<sub>2</sub>O (36%), m.p. 139—140°, b.p. 200—210°/1 mm.,  $[\alpha]_D^{25}$  +136° in CHCl<sub>3</sub>. All the (I) and part of the (II) are obtained as a 7:3 azeotrope, b.p. 59—61°/0.03 mm. Lack of oxidisable or acid groups and hydrolysis by boiling, dil. HCl to nepetalic acid (IV) proves the formula of (III). Only the acetate is obtained from (IV) by Ac<sub>2</sub>O, but AcCl in CCl<sub>4</sub> at room temp. gives also ~50% of (III). When kept, (IV) gives slowly (III). Distilling (IV) at 0.2 mm. gives 30% of (III), but at 1 atm. gives only (II), which is also obtained with H<sub>2</sub>O by distilling (III) at 1 atm. Of the ingredients only (II) has the excitant action on cats and lions characteristic of the oil. R. S. C.

**Saponins and sterols. VIII. Saponin of Dioscorea tokoro, Makino.** K. Fujii and T. Matsukawa (*J. Pharm. Soc. Japan*, 1936, 56, 408—414; cf. A., 1939, II, 161).—*Dioscorea* saponin is hydrolysed (5% H<sub>2</sub>SO<sub>4</sub>) to the sapogenin, C<sub>27</sub>H<sub>40-42</sub>O<sub>3</sub>, m.p. 198—200° (monoacetate, m.p. 190°; monobenzoate, m.p. 237°; dibromide, m.p. 127°), catalytically reduced and acetylated to dihydrodioscoreasapogenin acetate, m.p. 102°, yielding dihydrodioscoreasapogenin, m.p. 190°, which is reduced (Pd-Mg) to epidihydrodioscoreasapogenin, m.p. 205° (monoacetate, m.p. 206°). CH. ABS. (c)

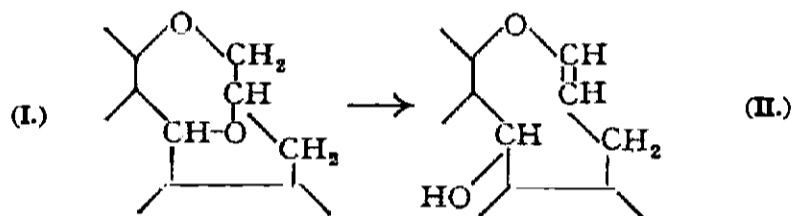
## VI.—HETEROCYCLIC.

**Condensation of  $\beta$ -cyclogeraniol with leucoisomaphthazarin.** M. D. Gates and F. Misani (*J. Amer. Chem. Soc.*, 1942, **64**, 1979—1980).—1 : 2 : 3 : 4- $C_{10}H_4(OH)_4$  (improved prep.),  $\beta$ -cyclogeraniol, and  $H_2C_2O_4$  in dioxan- $N_2$  at 65—70° in the dark give 2-hydroxy-3- $\beta$ -cyclogeranyl-1 : 4-naphthaquinone (poor yield), m.p. 135—135.5° (corr.), cyclised by conc.  $H_2SO_4$  to  $\beta$ -cyclogeranolapachone (I), m.p. 232—233.3° (corr.), identical with the so-called " $\beta$ -geranolapachone" obtained (A., 1942, II, 149) from 2-hydroxy-3-geranyl-1 : 4-naphthaquinone.



**Cannabis indica. XI. Alkali-soluble portion of American hemp resin.** (Mrs.) A. Madinaveitia, P. B. Russell, and A. R. Todd (*J.C.S.*, 1942, 628—630).—The alkali-sol. resin from American wild hemp has two components; one (I-RAB) is and the other (I-NRAB) is not extracted from alkaline solution with  $Et_2O$  (cf. Fulton, A., 1942, III, 771). These materials, with boiling MeOH, or with alkali, yield alkali-insol. resins, from which cannabidiol (I) and cannabinol (II) respectively have been isolated. The alkali-sol. portion of the resin may contain esters of (I) and (II) with a phenolic acid, which undergo fission with MeOH. This conclusion is supported by the properties of cannabinol *p*-carbomethoxybenzoate, m.p. 195°, and cannabidiol bis-*p*-carbomethoxybenzoate, b.p. ~130—150°/10<sup>-3</sup> mm.

**Reduction of tetramethylhaematoxylone.** P. Pfeiffer and W. Christleit (*J. pr. Chem.*, 1942, [ii], **160**, 315—322; cf. A., 1928, 426; 1938, II, 199).—Chromatographic analysis of the reduction product of tetramethylhaematoxylone gives tetramethylhaematoxylonol,  $C_{20}H_{22}O_7$ , m.p. 188°,  $\alpha$ -tetramethylisohaematoxylol,  $C_{20}H_{22}O_6$ , m.p. 196°, and  $\beta$ -tetramethylallohaematoxylol (I),  $C_{20}H_{22}O_6$ .



m.p. 150°. (I) and  $P_2O_5$  give the  $\alpha$ -form (II), m.p. 166°, which is acetylated and reduced by  $Ac_2O$ -NaOAc, giving a substance,  $C_{22}H_{24}O_7$ , m.p. 181—185°. Tetramethylhaematoxylol can be characterised (PhNCO at 100°) as the phenylcarbamate,  $C_{27}H_{28}O_7N$ , m.p. 203.5—206.5°.

A. T. P.

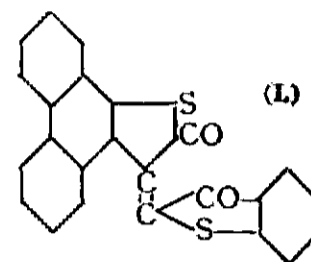
**Active principles of leguminous fish-poison plants. VII. Reduction of elliptone. VIII. Synthesis of dehydrotetrahydroelliptone and of dehydrotetrahydroalaccol. IX. Synthesis of furanisoelliptones related to rotenone.** S. H. Harper (*J.C.S.*, 1942, 587—593, 593—595, 595—598).—VIII. Reduction of *l*-elliptone (solvate with  $CHCl_3 \cdot CO_2H$ , m.p. 108°) in AcOH over  $PtO_2$  with  $H_2$  gives successively 1-dihydroelliptone (I), m.p. 191°,  $[\alpha]_D^{25} -132^\circ$  in  $C_6H_6$  (oxime, m.p. 250°; monoacetate, m.p. 208°), 1-dihydrodeoxyelliptone (II), m.p. 170°, octahydrodeoxyelliptone, m.p. 160° and 139°,  $[\alpha]_D^{25} -8^\circ$  in  $C_6H_6$ , and perhydroelliptone. Similar reduction of *dl*-elliptone affords *dl*-dihydroelliptone (III) (solvate,  $+0.5C_6H_6$ , m.p. 188°) and *dl*-dihydrodeoxyelliptone, m.p. 157—159°. (II) has been previously characterised as *l*-dihydroelliptone. Addition of I to (I) or (III) in EtOH-NaOAc yields dehydrodihydroelliptone (IV), m.p. 264°. Dehydroelliptone with Zn-KOH-EtOH leads to elliptic acid (V) (*Et* ester, m.p. 142°) and elliptol, m.p. 163° (*Me* ether, m.p. 137°). Cyclisation of (V) with NaOAc- $Ac_2O$  gives *Et* acetyl elliptate, m.p. 151—153°, and reduction ( $PtO_2-H_2$ ) of it affords dihydroelliptic acid (VI), m.p. 200° (*Me*, m.p. 149°, and *Et* ester, m.p. 147°), which is cyclised to a dimorph of (IV), m.p. 248—250°. Zn-KOH with (IV) forms (VI) and dihydroelliptol, m.p. 190°. *l*- or *dl*-Tetrahydroelliptone with NaOAc-I gives dehydrotetrahydroelliptone (VII), m.p. 260° (decomp.), which with Zn-KOH leads to tetrahydroelliptic acid (VIII), m.p. 202° (*Me* ester *Me* ether, m.p. 123°), and tetrahydroelliptol (+ solvent, EtOH- $H_2O$ ), m.p. 225°. *l*-Elliptone with  $AcOH-C_5H_{11}O \cdot NO$  affords elliptonone, m.p. 325°, which can be prepared from elliptol with  $Me_2C_2O_4$  and NaOAc. Reduction ( $PtO_2-H_2$ ) of *l*-isorenene (cf. Butenandt *et al.*, A., 1930, 477) gives an impure product, m.p. 168°, containing unreduced material, which is oxidised (I-NaOAc-EtOH) to dehydroisorotenone and 1-dihydrodeoxyisorotenone, m.p. 158°. Biological trials have shown that *l*-elliptone is, next to rotenone, the most toxic insecticidal substance to be isolated from *Derris* resin in an optically active form.

VIII. Condensation of Me 4 : 5-dimethoxy-2-cyanomethylphenoxyacetate, 2-ethylresorcinol, and  $ZnCl_2$  (Hoesch) gives *Me* tetrahydroelliptate, m.p. 185°, hydrolysed to (VIII), which is cyclised (NaOAc- $Ac_2O$ ) to (VII) and its O-*Ac* derivative, m.p. 253°. This confirms the structure assigned to elliptone. By the same condensation, using ethylphloroglucinol, *Me* tetrahydroalaccolate, m.p. 184°, is obtained, hydrolysed to the acid, m.p. 225°, which is cyclised to dehydrotetrahydroalaccol, m.p. 240° (decomp.), and its O-*Ac*,

derivative, m.p. 194—196°. It has not proved possible to compare these substances with those derived from natural sources.

IX. Derritol Me ether, Na, and  $HCO_2Et$  give derritol isoflavone (IX), m.p. 215°,  $[\alpha]_D^{25} -37^\circ$  in  $CHCl_3$ , hydrolysed (NaOH) to the ether and  $HCO_2H$ , and isomerised ( $AcOH-H_2SO_4$ ) to isoderritol isoflavone, m.p. 160°,  $[\alpha]_D^{25} \pm 0^\circ$  in  $CHCl_3$ , which is hydrolysed to isoderritol Me ether, m.p. 125°. This latter substance may be used for the synthesis of the isoflavone. Reduction ( $H_2-Pd-BaSO_4$ ) of (IX) leads to dihydroderritol isoflavone, m.p. 193°,  $[\alpha]_D^{25} -52^\circ$  in  $CHCl_3$ . Elliptol Me ether is similarly converted into elliptol isoflavanonol, m.p. 165°, which with AcOH yields the flavone, m.p. 185°, indicating that an intermediate OH-compound is formed in the isoflavone synthesis. These isoflavones are remarkable in giving a positive Durham test, previously regarded as sp. for the rotenoids. A method has been devised for the detection of the  $HCO_2H$  formed in their hydrolysis. This method has been applied to the "toxicarol isoflavone" isolated from crude toxicarol to establish conclusively its isoflavone nature and hence to support the formula previously assigned (cf. A., 1940, II, 356). F. R. S.

**Indigoid dyes. X.** P. C. Dutta and R. M. Sinha (*J. Indian Chem. Soc.*, 1942, **19**, 239—240; cf. A., 1936, 1518).—Phenanthra-9' : 10'-4 : 5-thiophen-2 : 3-dione and 2-hydroxythionaphthen in AcOH ( $CO_2$  passed through) when boiled, with addition of HCl, give phenanthra-9' : 10'-4 : 5-thiophen-3 : 1'-thionaphthenindigo (I), m.p. 290°. Similarly prepared are the 6'' : 7'', 4'' : 5'', and 5'' : 6''-benz-derivatives of (I); all melt at  $>295^\circ$ .



A. T. P.

**Dimeric thioketones.** H. Böhme, H. Pfeifer, and E. Schneider (*Ber.*, 1942, **75**, [B], 900—909).—Dimeric thioacetone (I) could not be obtained by the action of  $P_2S_5$  on  $COMe_2$  or from  $P_2S_5$  and  $COMe_2$  in boiling PhMe. Trithioacetone, b.p. 116—117°/15 mm., m.p. 24°, best obtained by passing  $H_2S$  into a well-cooled mixture of  $COMe_2$  and  $ZnCl_2$ , passes at 215° into  $Pr^{\beta}SH$ , identified as 2 : 4-dinitrophenyl  $Pr^{\beta}$  sulphide, m.p. 95°. Successive passage of HCl and  $H_2S$  into a well-cooled solution of  $CH_2ClAc$  in EtOH leads to 2 : 6-dimethyl-[2 : 6-endosulphido]dithian (I), b.p. 116—118°/14 mm., m.p. 50—51° (additive compound with  $HgCl_2$ , incipient decomp. 110°). (I) does not give an oxime, phenylhydrazone, or *p*-nitrophenylhydrazone and does not react with  $CH_2N_2$ , Grignard reagents, Na-Hg in EtOH, or Na in  $Et_2O$ . It is oxidised by  $KMnO_4$  in acid solution to a mixture of the corresponding trisulphone, decomp.  $>255^\circ$ , and an unidentified substance,  $C_6H_{10}O_4S_2$ , m.p. 227°. The structure of (I) is confirmed by comparison of its absorption spectrum in EtOH and  $CHCl_3$  with that of diacetyl sulphide, b.p. 126°/14 mm., m.p. 49°, obtained from  $CH_2ClAc$  and  $Na_2S \cdot 9H_2O$  in boiling  $COMe_2$ .  $CHPhClAc$  and HCl, then  $H_2S$  in well-cooled EtOH, afford 2 : 5-diphenyl-[1 : 4-dithien], m.p. 118—119° (Grote, A., 1924, i, 1322). 2 : 5-Diphenylthiophen, m.p. 155—156°, is obtained from  $(CH_2Bz)_2S$  and  $P_2S_5$  at 170°.

H. W.

**Nicotin-*p*-toluenesulphonamide.**—See B., 1942, III, 246.

**Action of acid anhydrides on acenaphthenone. II. Experiments in pyridine solution.** E. Ghigi (*Ber.*, 1942, **75**, [B], 764—778; cf. A., 1940, II, 179).—Prolonged action of  $Ac_2O$  in  $C_5H_5N$  on acenaphthenone in the dark affords 7-acetoxy-8-4'-pyridylacenaphthylene (I), m.p. 245—247° after softening, 1 : 8- $C_{10}H_6(CO_2H)_2$ , 7-hydroxy-8-1'-acetyl-1'-pyridinoacenaphthylene (II), m.p. 145—147°, 7-hydroxy-8-acetylacenaphthylene (III), 1 : 8- $C_{10}H_6(CO)_2O$  (IV), and MeCHO. The greater is the yield of (I), the smaller is the yield of (II). Prolonged contact of (III) with  $Ac_2O$  and  $C_5H_5N$  in the dark gives unchanged material and (IV). Under similar conditions 7-acetoxy-8-acetylacenaphthylene yields (III) and the acetate of (II) affords (I). (I) is transformed by boiling EtOH containing HCl into 7-hydroxy-8-4'-pyridylacenaphthylene hydrochloride, m.p. 262°, and by boiling 10% NaOH into 7-hydroxy-8-4'-pyridylacenaphthylene, colourless form (V), m.p. 185—192°, red variety (VI), m.p. 126—127° (also obtained directly by hydrolysis with boiling 95% EtOH).  $AcCl$  converts (VI) into (I) and (V) into resinous, non-cryst. products. At 130—140° and then at 200° (VI) passes into 8-4'-picolinoylnaphthalene-1-carboxylic acid (VII), m.p. 228—231°, identified as the picrate. A picrate, m.p. ~170°, of (VI) and a picrate (+ $H_2O$ ), m.p. 191°, and phenylhydrazone, m.p. 240°, of (V) are described. Distillation of (I) with Zn dust gives acenaphthene and 8 : 4'-pyridylacenaphthylene, identified as the picrate, m.p. 264—265°, and aurichloride, m.p. 205—210°. Alkaline  $KMnO_4$  oxidises (I) to (VII) [picrate, m.p. 235—240° (decomp.); corresponding hydroxamic acid, reddens at ~140°, m.p. 184—185°; N-oxide, m.p. 251—255°], converted by KOH at 160° into  $C_5H_5N$ , I- $C_{10}H_7 \cdot CO_2H$ , and isonicotinic acid (VIII). Decarboxylation of (VII) by Cu-bronze in boiling tetrahydronaphthalene leads to 1-naphthyl 4-pyridyl ketone (IX), m.p. 50—51° [picrate, m.p. 168—169°; phenylhydrazone, red leaflets, m.p. 100° (decomp.), and pale yellow needles, m.p. 232°; oxime, m.p. 195—196°], reduced (Cu and boiling 10%

HCl) to 1-naphthyl-4-pyridylcarbinol, m.p. 174—175° (picrate, m.p. 200°). KOH at 160° converts (IX) into 1-C<sub>10</sub>H<sub>7</sub>·CO<sub>2</sub>H and (VIII). CrO<sub>3</sub> in AcOH oxidises (I) to (VII). (I) and KOH at 160° give C<sub>5</sub>H<sub>5</sub>N, C<sub>10</sub>H<sub>8</sub>, and AcOH. AlCl<sub>3</sub> and (I) at 140° yield (III). Acenaphthenone does not give a ppt. after prolonged contact with Bz<sub>2</sub>O in C<sub>5</sub>H<sub>5</sub>N in the dark and is converted by (EtCO)<sub>2</sub>O under the same conditions into 7-propionyloxy-8-4'-pyridylacenaphthylene, m.p. 220° (with a little diacenaphthylidenedione), hydrolysed by 10% NaOH to (VI). H. W.

**Formation of pyrimidine rings.** II. Z. Földi, G. von Fodor, I. Demjén, H. Szekeres, and I. Halmos (*Ber.*, 1942, 75, [B], 755—763).—Traube's procedure (A., 1923, i, 1135) can frequently be improved by replacing the nitrile by the corresponding imino-ether. Gradual addition of NaOEt-EtOH to a solution of acetamidide hydrochloride (I) and CO<sub>2</sub>Et·CH<sub>2</sub>·C(OEt):NH<sub>2</sub>·HCl in EtOH gives 4-amino-6-hydroxy-2-methylpyrimidine (II), m.p. 293—294° (Ag salt), converted by boiling POCl<sub>3</sub> into 6-chloro-4-amino-2-methylpyrimidine, m.p. 189° (picrate, m.p. ~200°). This is unchanged by Zn powder in boiling EtOH-H<sub>2</sub>O and loses Cl only partly in presence of HCl; it is readily dehalogenated by H<sub>2</sub> in presence of Pd-C and HCl to 4-amino-2-methylpyrimidine, m.p. 205° (hydrochloride, m.p. 230°). A substance, C<sub>7</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub>, softens at 178°, m.p. 185—188°, is obtained as by-product in the prep. of (II) and is the main product from CN·CH<sub>2</sub>·CO<sub>2</sub>Et and (I). It appears to contain OEt which is not exactly determinable by Zeisel's method. It is neutral and unchanged by HCl or NH<sub>3</sub>. Attempts to convert CO<sub>2</sub>Et·C(CN):CH·OEt, CO<sub>2</sub>Et·CH(CN)·CH<sub>2</sub>·OMe, and OEt·CH(CN)<sub>2</sub> into their imino-ether hydrochlorides were unsuccessful. (I), CO<sub>2</sub>Et·CH(CN)·CH<sub>2</sub>·CO<sub>2</sub>Et (III), and NaOEt-EtOH afford Et 4-amino-6-hydroxy-2-methylpyrimidyl-5-acetate, m.p. >285°. (III) is transformed by HCl in abs. EtOH into the imino-ether hydrochloride, which is immediately condensed with (I) to 6:8-dihydroxy-2-methylpyrimazole (IV), m.p. >360°. It is converted by boiling POCl<sub>3</sub> into 6:8-dichloro-2-methylpyrimazole, m.p. 247—247.5°, which is unchanged by boiling 10% NaOH but transformed by 20% HCl at 100° into 4-amino-6-hydroxy-2-methylpyrimidine-5-acetic acid (hydrochloride), also obtained by the alkaline hydrolysis of (IV). The imino-ether bases from CN·CH<sub>2</sub>·CO<sub>2</sub>Et, m.p. 35—36°, and (III) [possibly Et 5-keto-2-ethoxy-Δ<sup>1</sup>-pyrroline-3-carboxylate], an oil, b.p. 100—118°/1 mm., are described. H. W.

**1:9-Pyrazoleanthrone-6:5-(N)-benzacridone.**—See B., 1942, II, 397.

**N-Arylmorpholones.**—See B., 1942, II, 396.

**Thiazoles.**—See B., 1942, II, 397.

**Preparation and reactions of 2-methylhexahydrobenzthiazole.** W. Dieterle (*Ber.*, 1942, 75, [B], 853—857).—2-Aminocyclohexanol is converted by Ac<sub>2</sub>O into its Ac<sub>2</sub> derivative, m.p. 115°, transformed by P<sub>2</sub>S<sub>5</sub> at 140° into 2-methylhexahydrobenzthiazole, b.p. 88—90°/9 mm. [ethiodide (I), m.p. 117—119°; methiodide, m.p. 167°]. Me of the quaternary salts is extremely reactive and undergoes condensation by the methods used for polymethine dyes. Those containing the hexahydrobenzthiazole ring are spectroscopically similar to those with the thiazoline ring. (I) and anilo-1-tetrahydroquinolylmethane are converted by cautious treatment with Ac<sub>2</sub>O into 2-β-tetrahydroquinolylvinylhexahydrobenzthiazole ethiodide, m.p. 182°, transformed by warm NaOH into tetrahydroquinoline and 2-aldehydomethylene-3-ethyloctahydrobenzthiazole, in which CHO is unusually reactive. H. W.

## VII.—ALKALOIDS.

**High-boiling bases of *Anabasis aphylla*, L.** E. Späth, F. Galinovsky, and M. Mayer (*Ber.*, 1942, 75, [B], 805—813; cf. Orekhov *et al.*, A., 1935, 97, 227).—The brown technical sulphate solution of the total bases is treated with conc. NaHCO<sub>3</sub> and Et<sub>2</sub>O, whereby mainly the bases (I) of high b.p. are removed; the residual aq. solution is made strongly alkaline with NaOH and extracted with Et<sub>2</sub>O, thereby giving chiefly anabasine and lupinine. Chromatographic separation (Al<sub>2</sub>O<sub>3</sub>) of (I) gives aphyllidine (II) and aphylline (III). (II) has m.p. 112—112.5°, [α]<sub>D</sub><sup>25</sup> +5.57° in MeOH, gives a methiodide, m.p. 225—227° (decomp.), and is hydrogenated (PtO<sub>2</sub> in N-HCl at 14°) to non-cryst. dihydroaphyllidine (IV). (II) is converted by successive treatments with boiling 5% HCl and HCl-EtOH into Et aphyllate (V), b.p. 150° (bath)/high vac., which gives a cryst. monohydrate, m.p. 76—77°, [α]<sub>D</sub><sup>25</sup> +25.30° in MeOH (platini-chloride, C<sub>17</sub>H<sub>30</sub>O<sub>2</sub>N<sub>2</sub>·H<sub>2</sub>PtCl<sub>6</sub>; corresponding Me ester monohydrate, m.p. 82—83°). (V) is hydrolysed to aphyllic acid, m.p. 218—221° (vac.; decomp.), which at 140—150°/high vac. passes into (III), [α]<sub>D</sub><sup>25</sup> +10.08° in MeOH, which could not be caused to crystallise; it gives a picrolonate, m.p. 233—234° (decomp.), and a methiodide, m.p. 219—221° (decomp.). Treatment of (IV) with boiling 3% HCl followed by esterification gives (V). (II) suffers ring-opening when boiled with 5% HCl but the esterified product is non-cryst. and becomes resinified in light petroleum within a few days. (V)

is also obtained from the residues left after removal of (II) and (III) from the sulphate liquor. H. W.

**Ergot alkaloids.**—See B., 1942, III, 278.

**Strychnos alkaloids.** CXVI. **Brucine-9-acetic acid and -9-nitrile.** H. Leuchs and H. J. Teuber (*Ber.*, 1942, 75, [B], 920—924).—ψ-Brucine (I) is converted by CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> in hot AcOH into brucine-9-acetic acid (II), m.p. 245—247° (vac.; slight decomp.), [α]<sub>D</sub><sup>25</sup> −64° in H<sub>2</sub>O [perchlorate (III), (anhyd.) m.p. 240—250° (vac.), (hydrate) softens at 190° and foams and becomes discoloured at 220°; Me ester perchlorate, m.p. 191—194° (vac.; decomp.)]. Oxidation of (III) by 5N-HNO<sub>3</sub> at 0° gives a red quinone solution reduced by SO<sub>2</sub> to the quinol, C<sub>23</sub>H<sub>24</sub>O<sub>6</sub>N<sub>2</sub> (perchlorate), and oxidised by HClO<sub>4</sub> at 50° to the nitroquinone, C<sub>23</sub>H<sub>23</sub>O<sub>6</sub>N<sub>3</sub> (perchlorate), reduced to the nitroquinol, C<sub>23</sub>H<sub>25</sub>O<sub>6</sub>N<sub>3</sub> (perchlorate). (II) is reduced (PtO<sub>2</sub> in H<sub>2</sub>O) to dihydrobrucineacetic acid, m.p. 282—284°. (III) and PhCHO in boiling NaOMe-MeOH afford benzylidenebrucineacetic acid [perchlorate monohydrate, becomes discoloured at 240° and gives a resin at 305° (vac.)]. When heated at its m.p. (II) yields CO<sub>2</sub> and 9-methylbrucine [perchlorate, m.p. 260—300° (decomp.)]. (I) and KCN in AcOH at 20° and subsequently at 100° afford brucine-9-nitrile (IV), m.p. 228—232° (vac.) (hydrochloride; perchlorate), which is not hydrolysed by boiling 2N-NaOH or 2N-HClO<sub>4</sub>. It is not greatly attacked by Zn-Hg in 6N-HCl but is reduced by H<sub>2</sub> in presence of Pt and N-HCl to 9-aminomethylidihydrobrucine, m.p. (hydrated) 120—123° (vac.), (anhyd.) foams at 120—140° and becomes transparent at 160° [diperchlorate, m.p. 220—265°; Ac derivative, softens at 250°, m.p. 257—260° (vac.)]. (IV) is oxidised by KMnO<sub>4</sub> in COMe<sub>2</sub> to brucinonitrile, softens at 260°, m.p. 275—280° (vac.; decomp.). (IV) is converted by 2N-HClO<sub>4</sub> and 5N-HNO<sub>3</sub> followed by SO<sub>2</sub> at 20° into the quinol, C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>N<sub>3</sub> (perchlorate); if the solution is heated to 50° and then reduced the product is the nitroquinol hydrate, C<sub>22</sub>H<sub>22</sub>O<sub>7</sub>N<sub>4</sub> (perchlorate). H. W.

**Alkaloid of *Berberis umbellata*, Wall.** II. R. Chatterjee (*J. Indian Chem. Soc.*, 1942, 19, 233—238; cf. A., 1941, II, 23).—Umbellatine (I), C<sub>4</sub>H<sub>8</sub>(OH)<sub>2</sub>(CH<sub>2</sub>O<sub>2</sub>)(NMe)(OMe)<sub>2</sub>(OH)<sub>2</sub> [nitrate, m.p. >250°; sulphate, m.p. 274° (decomp.); picrate, m.p. 232° (decomp.); Ac<sub>2</sub> derivative, m.p. 193° (decomp.) (shrinks at 187°); does not form an oxime or semicarbazone], occurs in the Himalayan *Berberis* sp., and is probably related to berberine in structure. A comparison of the absorption curves and properties of the two compounds indicates close similarity. (I) probably possesses a methylenedioxy-tetrahydroisoquinoline skeleton; it contains an imino-Me, and 4 active H (probably from 4 OH). Hydrogenation (Pd-C in MeOH) affords dihydro-, chars without melting, and tetrahydro-umbellatine, m.p. 213—215° (decomp.). MeI converts (I) into a methiodide, but Me<sub>2</sub>SO<sub>4</sub>-aq. KOH yields the Me ether, m.p. 265°. A. T. P.

**Alkaloids of the fruit of *Solanum xanthocarpum*.** B. L. Manjunath and M. Shadaksharaswamy (*J. Mysore Univ.*, 1942, 3, B, 117—121; cf. A., 1937, II, 435; 1938, II, 35, 299).—From the EtOH extract of the defatted dried fruits of *S. xanthocarpum* have been isolated glucose, rhamnose, galactose, and solanine-s, m.p. 279° (shrinks at 273°, decomp. 290°) [platini-chloride, m.p. 155° (decomp.)], hydrolysed (H<sub>2</sub>SO<sub>4</sub>) to solanidine, m.p. 197.5°, [α]<sub>D</sub><sup>25</sup> +113.5° in CHCl<sub>3</sub> (Bz<sub>3</sub> derivative, m.p. 227°; Me<sub>3</sub> ether methiodide, m.p. 233—234°), which contains neither OMe nor NMe groups. A. Li.

**H. Wieland's work on natural nitrogenous substances (alkaloids and pterins).** C. Schöpf (*Naturwiss.*, 1942, 30, 359—373).—A review. F. O. H.

## VIII.—ORGANO-METALLIC COMPOUNDS.

**Oxidation of *n*-butylboron.**—See A., 1942, I, 400.

**Mercurated aliphatic ketones.**—See B., 1942, III, 223.

**Mercuriphenyl derivative.**—See B., 1942, III, 224, 246.

**Mercurated 3-nitro-6-alkylphenols.**—See B., 1942, III, 223.

## IX.—PROTEINS.

**Determination of mol. wt. and particle form of some breakdown products of gelatin by precipitation-titration.** B. Jirgensons (*J. pr. Chem.*, 1942, [ii], 160, 21—32).—Mol. wts. of 1000—30,000 have been found by pptn.-titration in agreement with other methods for breakdown products of gelatin. The dependence of precipitability on concn. indicates a long chain form for the particles. F. J. G.

**Application of acidic and basic alumina columns to analysis of protein hydrolysates.** T. Wieland (*Naturwiss.*, 1942, 30, 374—376).—The method is based on the adsorption of only aminodicarboxylic acids by acidic (HCl-treated) Al<sub>2</sub>O<sub>3</sub> and of only diamino-carboxylic acids by untreated Al<sub>2</sub>O<sub>3</sub>, neutral NH<sub>2</sub>-acids and histidine being unadsorbed. The Na salts of NH<sub>2</sub>-acids in 80% EtOH are adsorbed on the acidic Al<sub>2</sub>O<sub>3</sub> and can be separated from glucose,

which is not adsorbed under similar conditions. The application of the method to the hydrolysates of caseinogen and other proteins yielded by boiling with 20%  $\text{H}_2\text{SO}_4$  for 20 hr. or with conc.  $\text{HCl}$  for 12 hr. is described. Tryptophan is partly degraded during the hydrolysis, whilst the yield of hydroxyglutamic acid (from caseinogen) is greater with the  $\text{HCl}$  hydrolysis than with the longer  $\text{H}_2\text{SO}_4$  hydrolysis. F. O. H.

**Preparation and properties of protein sols. II. Sols with *l*-histidine, *d*-arginine, *l*-proline, and *l*-hydroxyproline.**—See A., 1943, I, 15.

**Histidine content of hæmoglobin.**—See A., 1942, III, 874.

## X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

**Isolation of three new bitter principles from neem oil.** S. Siddiqui (*Current Sci.*, 1942, 11, 278—279).—Fractionation by solvent methods yielded *nimbin*,  $\text{C}_7\text{H}_{10}\text{O}$ , m.p.  $205^\circ$  (0.1% of the oil), *nimbini*, m.p.  $192^\circ$  (0.01%), and *nimbidi*, m.p.  $90$ — $100^\circ$  (1.1%), all neutral,  $\text{H}_2\text{O}$ -insol., and bitter-tasting in aq.-EtOH suspension. R. L. E.

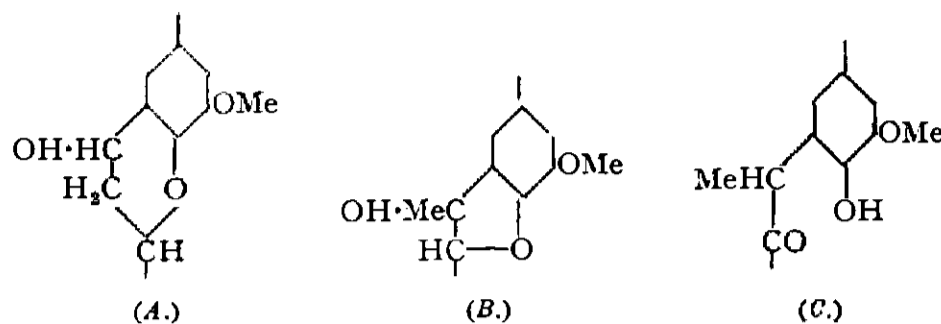
**Primula saponin.** A. Margot and T. Reichstein (*Pharm. Acta Helv.*, 1942, 17, 113—140).—The extraction is described of a saponin (as Na salt) from defatted powdered primula root; the yield is 4.1% from *P. officinalis*, and 2.3% from *P. elatior*. The free saponin has m.p.  $235$ — $237^\circ$  (decomp.),  $[\alpha]_D^{19} - 34.8^\circ$  in MeOH (*P. officinalis*), or m.p.  $240$ — $241^\circ$  (decomp.),  $[\alpha]_D^{17} - 31.8^\circ$  (*P. elatior*). The yield of Me ester (with  $\text{CH}_3\text{N}_2$  in  $\text{Et}_2\text{O}$ ),  $\text{C}_{19}\text{H}_{30}\text{O}_{19}$ , m.p.  $314$ — $315^\circ$  (decomp.),  $[\alpha]_D^{14} - 35.3^\circ$ , from the latter is  $>3$  times that from the former. The Me ester acetate has m.p.  $205$ — $209^\circ$ ,  $[\alpha]_D - 16.4^\circ$  to  $-17.6^\circ$ . Hydrolysis of both saponins yields: *genin A*, m.p.  $248$ — $250^\circ$ ,  $[\alpha]_D^{15} + 16.6^\circ$  [*diacetate* (I), m.p.  $220$ — $221^\circ$ ,  $[\alpha]_D^{15} - 31.2^\circ$  in  $\text{CHCl}_3$ ; *triacetate*, m.p.  $153$ — $156^\circ$ ,  $[\alpha]_D^{23} - 8.4^\circ$  in  $\text{COMe}_2$ ]; *genin B*, m.p.  $248$ — $255^\circ$ ,  $[\alpha]_D^{15} + 62.4^\circ$  in EtOH [*diacetate* (II), m.p.  $216$ — $218^\circ$  (decomp.),  $[\alpha]_D + 64.9^\circ$  in  $\text{CHCl}_3$ ; no triacetate formed]. *Diacylgenin C* (III), m.p.  $267$ — $271^\circ$ ,  $[\alpha]_D^{15} + 5.5^\circ$  in  $\text{CHCl}_3$ , is separated by fractional dissolution from the acetylation products of the genin; it yields by alkaline hydrolysis *genin A*. Oxidation ( $\text{CrO}_3$  in  $\text{AcOH}$ ) of (I) yields a compound,  $\text{C}_{34}\text{H}_{50}\text{O}_6$ , m.p.  $262$ — $265^\circ$ ,  $[\alpha]_D - 3.1^\circ$  in  $\text{CHCl}_3$ . Similarly (II) yields a substance,  $\text{C}_{36}\text{H}_{54}\text{O}_7$ , m.p.  $285$ — $293^\circ$  (decomp.), and (III) two substances, m.p.  $168$ — $172^\circ$  and  $265$ — $271^\circ$ . Oxidation (Br) of the  $\text{COMe}_2$ -sol. carbohydrate portion yields *d*-galactose and *d*-glucose. From the products of aq.-EtOH- $\text{H}_2\text{SO}_4$  hydrolysis of the saponin an EtOH-insol. Ba salt of a uronic acid was obtained; oxidation (Br) of the free acid yielded two fractions, one which gave a sparingly sol. K salt, and the other a quinine salt, m.p.  $181$ — $183^\circ$  (decomp.), which could not be identified. P. G. M.

**Constituents of hinokiol. VIII. Synthesis of matairesinol dimethyl ether from hinokinin.** S. Keimatsu and T. Ishiguro (*J. Pharm. Soc. Japan*, 1936, 56, 399—404; cf. A., 1937, II, 21).—Hinokinin with  $\text{KOH}$ -MeOH at  $175$ — $180^\circ$  for 6—7 hr. gave a compound, m.p.  $114$ — $116^\circ$ , and a phenol (I), acetylation and/or methylation of which gave matairesinol Me<sub>2</sub> ether, identified by m.p.,  $(\text{NO}_2)_2$ - and  $\text{Br}_2$ -compounds. Ethylation ( $\text{Et}_2\text{SO}_4$ ) and hydrolysis ( $\text{KOH}$ ) of (I) gave  $\alpha\beta$ -bis-(3 : 4-diethoxybenzyl)butyrolactone. CH. ABS. (c)

**Claviformin** ( $\text{C}_9\text{H}_{10}\text{O}_5$ ), m.p.  $110^\circ$ .—See A., 1942, III, 937.

**Lignin. L. Acetic acid-lignin.** K. Freudenberg and E. Planckenhorn (*Ber.*, 1942, 75, [B], 857—867).—Repeated treatment of pine wood with a boiling mixture of  $\text{AcOH}$  and aq.  $\text{MgCl}_2$  removes the whole of the lignin as "acetic acid-lignin" (I), freely sol. in aq. alkali hydroxide,  $\text{COMe}_2$ ,  $\text{AcOH}$ ,  $\text{C}_5\text{H}_5\text{N}$ , and undiluted  $\text{N}_2\text{H}_4$ ,  $\text{H}_2\text{O}$ , insol. in  $\text{H}_2\text{O}$  and carbonate, scarcely sol. in abs. EtOH, and partly sol. in aq. EtOH. Alkali removes 10% of Ac leaving a product sol. in aq. alkali hydroxide,  $\text{AcOH}$ , and  $\text{C}_5\text{H}_5\text{N}$  but insol. in  $\text{H}_2\text{O}$  and carbonate, almost insol. in aq. EtOH or anhyd.  $\text{COMe}_2$ . The characteristic solubilities are therefore proper to the fundamental Ac-free product. Isolated cuproxam-lignin (II) (insol. in alkali) is transformed by  $\text{AcOH}$ -aq.  $\text{MgCl}_2$  into (I) with the same properties. These, however, are foreign to the native lignin since hydrolysed (I) from wood or (II) cannot be changed by hot 1%  $\text{H}_2\text{SO}_4$  into an alkali-insol. product resembling (II). (II) appears to be more closely related than the alkali- or organosolve- (III)-lignin to native lignin. It is brought into solution by  $\text{HSO}_3^-$  and is followed in this respect by laboratory "HCl-lignin" (IV) and Tornesch lignin which are dissolved with difficulty or not at all. Technical (IV) has been further changed and is partly sol. in alkali owing to partial demethylation. The alkali- and organosolve-lignins are little affected by  $\text{HSO}_3^-$  even after pre-treatment with  $\text{SO}_3$ . Lignin in wood and (III) have thermoplasticity in common but this property is not

shown by (II); it appears to depend on the slight degree of condensation of lignin in wood. Determination of phenolic OH in lignin cannot be effected potentiometrically and the regulated Ac elimination from (I) gives difficultly interpretable results. Some information is derived from analysis of the Na salts obtained by the action of  $\text{NaOAlk}$  on hydrolysed (I) in an org. medium but the most satisfactory process consists of the treatment of the toluene-sulphonates with anhyd.  $\text{N}_2\text{H}_4$ . The increase of phenolic OH from 0.7% in (II) to 3.3% in deacetylated (I) does not correspond with



an increase in total OH and is accounted for on the hypothesis that units of type A are unchanged by  $\text{AcOH}$ - $\text{MgCl}_2$  followed by hydrolysis whereas units of type B pass into those of type C. Very little vanillin is obtained by oxidation of (I) with  $\text{PhNO}_2$ , and even in presence of  $\text{Co}(\text{OH})_2$  the yield is  $\ll$  that from untreated lignin. This is ascribed to the inability of C and ability of B to yield the CHO group. H. W.

## XL—ANALYSIS.

**Gas-fired furnace for semi-micro-determination of carbon and hydrogen.** H. A. Paget (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 764—766).—The novel features of the furnace are Ag sleeves, for distribution of heat, on the combustion tube sections, and screens for the sections to prevent premature volatilisation of the test substance. J. D. R.

**Isothermal diffusion method of preparing highly purified microchemical reagents.**—See A., 1943, I, 26.

**Lower aliphatic alcohols. Application of the Zerevitinov determination.** W. Hollyday and D. L. Cottle (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 774—775).—Apparatus for determination of lower aliphatic alcohols by the Zerevitinov method is described in detail. *iso*-Amyl ether is used as solvent for the alcohol and the Grignard reagent. The concn. of the alcohol in the solvent should be such that no appreciable ppt. of Mg alkoxyiodide is formed. J. D. R.

**Determination of alkoxy groups in cellulose ethers.** E. P. Samsell and J. A. McHard (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 750—754).—A detailed description is given of the construction and operation of a modified Zeisel apparatus for the Vieböck determination of OEt and OMe in cellulose ethers. The use of a solvent in addition to the HI is not advisable except in the cases of very resistant substances, when  $\text{PhOH}$  or  $(\text{EtCO})_2\text{O}$  may be used. J. D. R.

**New reaction for the investigation of amino-acids.** A. Barreto (*Rev. Quim. Ind.*, 1942, 11, 275).—1 c.c. of a neutral solution containing  $\text{NH}_2$ -acids (I) with 1 c.c. of 15—20% neutral  $\text{C}_6\text{Cl}_5\text{ONa}$  and 1 c.c. of neutral 40%  $\text{CH}_2\text{O}$  gives a white ppt. of  $\text{C}_6\text{Cl}_5\text{OH}$ . (I) may be determined as  $\text{C}_6\text{Cl}_5\text{OH}$  in 1 c.c. of 0.5—1.0% solution by adding 2 c.c. of neutral 20%  $\text{C}_6\text{Cl}_5\text{ONa}$  and 2 c.c. of neutral 40%  $\text{CH}_2\text{O}$ . F. R. G.

**Step-photometric determination of oestrogenic stilbenes.** E. Huf and G. Widmann (*Z. physiol. Chem.*, 1942, 274, 88—95).—4 : 4'-Di-hydroxy- $\alpha\beta$ -diethylstilbene gives a yellow-red colour with  $p$ - $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  in borate-buffered solution (pH 12) which, under defined conditions, can readily be used for its determination with an accuracy of  $\pm 10\%$ . The process can be extended to esters (oil- or  $\text{H}_2\text{O}$ -sol.) if they are hydrolysed before addition of the reagent. Directions are also given for the determination of oestrogenic stilbenes in oil or tablets, from which they are extracted by MeOH. H. W.

**Wing pigments of butterflies. XIII. Detection and determination of leucopterin.** P. Decker (*Z. physiol. Chem.*, 1942, 274, 223—230).—Leucopterin (I) is detected and approx. determined by measurement of its blue fluorescence in alkaline solution. It could not be detected in human urine, snake excrement, or guano, in which the respective limits of sensitiveness are  $<1$  mg. per l.,  $<0.02\%$ , and  $<0.3\%$ . The grub of the clothes moth contains 0.01% of (I). (I) is sol. in  $\sim 10^6$  parts of  $\text{H}_2\text{O}$  at  $20^\circ$ . H. W.

**Determination of protein by biuret and Greenberg methods.**—See A., 1943, III, 76.

# BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

## A., II.—Organic Chemistry

FEBRUARY, 1943.

### I.—ALIPHATIC.

**Products from the Wurtz reaction. Mechanism of their formation.** A. Saffer and T. W. Davis (*J. Amer. Chem. Soc.*, 1942, **64**, 2039—2043).—At 320°/200 mm., Mel, EtI, or Mel-EtI with Na gives complex mixtures containing H<sub>2</sub>, C, saturated and unsaturated hydrocarbons (much CH<sub>4</sub> from Mel or C<sub>2</sub>H<sub>6</sub> from EtI). The results are explained as due to formation of alkyl radicals, which react mainly with excess of halide. Secondary radicals disappear by interaction with each other or Na. R. S. C.

**Tracer studies with radioactive hydrogen. (A) Synthesis of labelled methyl iodide. (B) Menschutkin reaction.**—See A., 1943, I, 39.

**Photo-oxidation of methyl iodide.**—See A., 1943, I, 40.

**Common basis of intramolecular rearrangements. IX. Formation of cyclopropanes from monohalides. III. Action of sodium alkyls on aliphatic chlorides. Relation to the Wurtz reaction.** F. C. Whitmore and H. D. Zook (*J. Amer. Chem. Soc.*, 1942, **64**, 1783—1785; cf. A., 1942, II, 83).—HgEt<sub>2</sub> (excess) and Na in *n*-C<sub>8</sub>H<sub>17</sub>-N<sub>2</sub> at 25° give NaEt (80%) and 5—8% Na-Hg. NaEt and *n*-C<sub>8</sub>H<sub>17</sub>Cl at -10° to 0° give (a) by coupling *n*-C<sub>8</sub>H<sub>17</sub> (40%) and (b) CH<sub>2</sub>:CHBu<sup>a</sup> (46%) + C<sub>2</sub>H<sub>6</sub> (52%). NaPr<sup>a</sup> (prep. from HgPr<sup>a</sup><sub>2</sub> in *n*-C<sub>8</sub>H<sub>17</sub>-N<sub>2</sub>) and CH<sub>2</sub>Bu<sup>a</sup>Cl do not react at <50° but at 50—60° give 1:1-dimethylcyclopropane (75%), C<sub>3</sub>H<sub>8</sub> (70%), Bu<sup>a</sup>Bu<sup>a</sup> (4%), and C<sub>3</sub>H<sub>6</sub> (5%); probably formed by decomp. of NaPr<sup>a</sup>. CH<sub>2</sub>Bu<sup>a</sup>Cl does not react with 6% Na-Hg. NaAlk thus reacts partly as a base, removing HHal from the halide, and this is their effect when they are formed in the Wurtz reaction. The olefine is derived solely from the halide and the simple paraffin from the NaAlk. R. S. C.

**Higher hydrocarbons. II. Five λ-substituted heneicosanes.** F. C. Whitmore, J. N. Cosby, W. S. Sloatman, and D. G. Clarke (*J. Amer. Chem. Soc.*, 1942, **64**, 1801—1803; cf. A., 1942, II, 341).—*n*-C<sub>12</sub>H<sub>25</sub>·MgBr (I) and *n*-C<sub>5</sub>H<sub>11</sub>·CO<sub>2</sub>Et (1.07 mols.) give *n*-C<sub>5</sub>H<sub>11</sub>·C(C<sub>12</sub>H<sub>25</sub>-*n*)<sub>2</sub>·OH (II), b.p. 225—229°/1 mm., and some *n*-C<sub>10</sub>H<sub>22</sub> and hexadecan-η-one. Dehydration of (II) by CuSO<sub>4</sub>-N<sub>2</sub> at 160—180°, purification of the olefine by SiO<sub>2</sub> gel, and then hydrogenation over Ni at 120°/1100 lb. gives λ-*n*-amyl-*n*-heneicosane, m.p. -9.1°, b.p. 192°/1 mm. λ-*α*-Ethyl-*n*-propyl-, b.p. 187°/1 mm., and λ-cyclopentyl-*n*-heneicosane, m.p. -12.7°, b.p. 186°/1 mm., are similarly prepared using ~2 mols. of the appropriate ester. MeOBz (3 mols.) and (I) in Et<sub>2</sub>O give, after dehydration of the carbinol, λ-phenyl-Δ<sup>α</sup>-*n*-heneicosene, b.p. 203°/1 mm., hydrogenated in presence of very active Ni at room temp./1800 lb. to λ-phenyl-, m.p. 20.8°, b.p. 204°/1 mm., or in presence of Ni at 150°/1500—1800 lb. to λ-cyclohexyl-*n*-heneicosane, m.p. -7.2°, b.p. 209°/1 mm. Et cyclopentanecarboxylate, b.p. 171.9°/737 mm., is prepared (48.5%) from Mg cyclopentyl bromide and Et<sub>2</sub>CO<sub>3</sub> in Et<sub>2</sub>O at 0°. *n*, *d*, and *η* are recorded for the hydrocarbons. Purities are >95%. R. S. C.

**Allylic rearrangements. XIII. Kinetics and mechanisms of the conversion of crotyl and methylvinylcarbinyl chlorides into acetates and ethyl ethers.** J. D. Roberts, W. G. Young, and S. Winstein (*J. Amer. Chem. Soc.*, 1942, **64**, 2157—2164; cf. A., 1942, II, 293).—Bimol. interaction of CHMe:CH·CH<sub>2</sub>Cl (I) or CH<sub>2</sub>:CH·CHMeCl (II) with OEt' or OAc' gives only the normal product and solvolytic (S<sub>N</sub>1) reaction gives mixtures. The first type can be induced without the latter. Interaction of (I) with NaOEt in EtOH is of the second order, little changed by adding a little H<sub>2</sub>O. Solvolysis of (I) with EtOH at 25° is of the first order, *k*<sub>1</sub> (1.84 × 10<sup>-4</sup>) of which is much increased by H<sub>2</sub>O (12.3 × 10<sup>-4</sup> in presence of 5.35 mols. of H<sub>2</sub>O per l.). 99% pure Et ether is obtained from 0.7M-(I) and 0.9M-NaOEt, and >96%-pure Et ether from 1.3M-(II) and 1.8M-NaOEt. With KOAc or diphenylguanidinium acetate in AcOH, (I) or (II) gives mixed acetates, the kinetics being those of mixed-order reactions, but KOAc-Ac<sub>2</sub>O at 100° reacts homogeneously with (I) and NEt<sub>4</sub>·OAc-COMe<sub>2</sub> at 58° similarly with (II). R. S. C.

**Dehydration Δ<sup>αα</sup>-hexadien-γ-ol to Δ<sup>αα</sup>-hexatriene and Δ<sup>1:3</sup>-cyclohexadiene.** L. W. Butz (*J. Amer. Chem. Soc.*, 1942, **64**, 1978—1979).—Dehydration (conditions: A., 1940, II, 182) of CH<sub>2</sub>:CH·CH<sub>2</sub>:CH(OH)·CH:CH<sub>2</sub> gives some Δ<sup>1:3</sup>-cyclohexadiene (I), since with (·CH·CO)<sub>2</sub>O at 30° the product gives the endoethylene-

tetrahydrophthalic anhydride, m.p. 147°, also obtained from pure (I). However, the amount of (I) formed varies uncontrollably. R. S. C.

**Synthesis of higher alcohols from water-gas under pressure.**—See B., 1942, II, 393.

**Preparation and properties of polyethoxyethanes and their bromo-derivatives.** S. M. McElvain and P. M. Walters (*J. Amer. Chem. Soc.*, 1942, **64**, 1963—1965).—CMe(OEt)<sub>3</sub> and Br (1 mol.) in C<sub>6</sub>H<sub>5</sub>N at ~30°, later 60—70°, give 53% of CHBr<sub>2</sub>·C(OEt)<sub>3</sub>, b.p. 102—104°/8 mm., converted by boiling KOEt-EtOH into CH<sub>2</sub>Br·C(OEt)<sub>3</sub> and thence (excess of alkali or separate experiment) CMe(OEt)<sub>3</sub>·CHMe(OEt)<sub>2</sub> and Br in C<sub>6</sub>H<sub>5</sub>N at 10—15° give CH<sub>2</sub>Br·CH(OEt)<sub>2</sub> (23%) and CHBr<sub>2</sub>·CH(OEt)<sub>2</sub> (29%). OEt·CH<sub>2</sub>·CH(OEt)<sub>2</sub> with Br in C<sub>6</sub>H<sub>5</sub>N at 65° gives a mixture, including 15% of (OEt)<sub>2</sub>CH·CHO, b.p. 79°/12 mm., but in absence of a solvent suffers fission to EtBr (0.85), H<sub>2</sub>O (0.97), EtOH (0.75), and CHBr<sub>2</sub>·CH(OEt)<sub>2</sub> (0.25 mol.). (CH<sub>2</sub>·OEt)<sub>2</sub> and Br at 80° or in C<sub>6</sub>H<sub>5</sub>N at 65° give mixtures. CHBr<sub>2</sub>·CH(OEt)<sub>2</sub> and boiling KOH-EtOH give CHBr·C(OEt)<sub>2</sub> (62.5%), b.p. 72—73°/11 mm.; CHCl<sub>2</sub>·CH(OEt)<sub>2</sub> gives CHCl·C(OEt)<sub>2</sub> (60%), b.p. 57—58°/10 mm. OEt·CH<sub>2</sub>·CO·NH<sub>2</sub>, m.p. 82—83°, b.p. 225—230°, and P<sub>2</sub>O<sub>5</sub> at 150—180° give OEt·CH<sub>2</sub>·CN (60%), b.p. 133—134°. Et<sub>3</sub> ethoxyorthoacetate (prep. from CH<sub>2</sub>Cl·CN), b.p. 69—70°/10 mm., 180—181°/740 mm., is largely decomposed by Br in C<sub>6</sub>H<sub>5</sub>N at 80°. OEt·CHBr·CH(OEt)<sub>2</sub> and KOEt-EtOH give CHBr·C(OEt)<sub>2</sub> (cf. A., 1938, II, 4). R. S. C.

**Tracer studies with radioactive carbon. Synthesis and oxidation of three-carbon acids.**—See A., 1943, I, 39.

**Fats from fatty acids having an odd number of carbon atoms.** W. Keil (*Z. physiol. Chem.*, 1942, **274**, 175—185).—See A., 1943, III, 131. CH<sub>3</sub>EtBu<sup>a</sup>·CH<sub>2</sub>·OH and HBr at 100—130° give the bromide, b.p. 72—75°/10 mm., converted by, successively, CHNa(CO<sub>2</sub>Et)<sub>2</sub>-EtOH, boiling KOH-EtOH, and heat at 180° into γ-ethyl-*n*-octoic acid, b.p. 142—143°/10 mm. The derived Et ester, b.p. 108—110°/10 mm., with H<sub>2</sub>-Cu chromite at 270° gives CH<sub>3</sub>EtBu<sup>a</sup>·[CH<sub>2</sub>]<sub>2</sub>·OH, b.p. 108—110°/10 mm., and thence, as above, the bromide (I), b.p. 104—106°/10 mm., and ε-ethyl-*n*-decoic acid, a liquid. With boiling KCN-KI-EtOH, (I) gives the nitrile, b.p. 126—128°/14 mm., which with HCl-EtOH and then NaOH gives δ-ethyl-*n*-nonoic acid, b.p. 163—166°/17 mm. (Et ester, b.p. 126—130°/17 mm.). *n*-Decaldehyde and MgMeBr-Et<sub>2</sub>O give *n*-undecan-β-ol and thence the bromide, b.p. 128°/15 mm., *n*-C<sub>8</sub>H<sub>17</sub>·CHMe·CH(CO<sub>2</sub>Et)<sub>2</sub>, b.p. 150—152°/2 mm., and, by aq. NaOH at 130—150° and then decarboxylation at 180°, β-methyl-*n*-dodecoic acid, b.p. 125—130°/16 mm. *n*-Octaldehyde gives similarly *n*-nonan-β-ol, the bromide, b.p. 116—118°/38 mm., Me β-methyl-*n*-decoate, b.p. 110—113°/18 mm. (by H<sub>2</sub>-Cu chromite at 280°/180 atm.; then HBr), γ-methyl-*n*-decyl bromide, b.p. 120—124°/20 mm., and δ-methyl-*n*-dodecoic acid, b.p. 132°/10.6 mm. R. S. C.

**Action of fatty acids on copper.**—See A., 1943, I, 40.

**Preparation of orthoesters.** S. M. McElvain and J. W. Nelson (*J. Amer. Chem. Soc.*, 1942, **64**, 1825—1827).—MgRX and C(OEt)<sub>3</sub> give CR<sub>2</sub>(OEt)<sub>2</sub> and CR<sub>3</sub>·OEt with very little CR(OEt)<sub>3</sub>. Prep. of CR(OEt)<sub>3</sub> is best (59—78%) effected by treating OEt·CR·NH<sub>2</sub>·HCl (A) with EtOH (15 mols.) in presence of Et<sub>2</sub>O (1—3 vols.; optimum stated for Me-Bu) at the b.p. (39—46°). If R is branched, the yield is lower (Pr<sup>β</sup> 27—30, Bu<sup>β</sup> 21—23%). However, CH<sub>2</sub>Cl·C(OEt)<sub>3</sub> is best prepared by EtOH alone at ~40°. The decomp., (A) → RCO·NH<sub>2</sub> + EtCl, becomes appreciable only at higher temp. (80—80°). Prep. of (A) from RCN and HCl-EtOH is described. Et<sub>3</sub> orthoacetate, b.p. 144—146°/740 mm., -propionate, b.p. 70—72°/32 mm., -*n*-, b.p. 58—59°/7 mm., and -iso-butylate, b.p. 50—51°/7 mm., -*n*-, b.p. 49—50°/3 mm., and -iso-valerate, b.p. 57—59°/7 mm., and -chloroacetate, b.p. 68—70°/10 mm., are prepared. R. S. C.

**Preparation of high-molecular derivatives of aliphatic hydroxy-monocarboxylic acids.**—See B., 1942, II, 394.

**Production of purified sodium lactate.**—See B., 1942, II, 394.

**Purification of ethyl lactate.**—See B., 1942, II, 394.

**Loco weeds. V. Constituents of *Astragalus earlei*.** A. Stempel and R. C. Elderfield (*J. Org. Chem.*, 1942, **7**, 432—443; cf. A., 1940, II, 185; III, 462).—The substances previously called "a-

and  $\beta$ -earleine'' are identified as betaine and choline respectively. The reported pptn. of the active constituent of *A. earlei* by phosphotungstic acid is probably due to adsorption on the ppt. Reinecke salt ppts, a highly active fraction from which a cryst. substance has been isolated and also ppts. bases with a strong ninhydrin reaction. A *dihydroxyvalerolactone*, m.p. 52—53°,  $[\alpha]_D^{25}$  -64.7° in  $H_2O$  (*diacetate*, m.p. 86—87°,  $[\alpha]_D^{25}$  -7.09° in  $CHCl_3$ ; *phenylhydrazide* of the OH-acid corresponding to the lactone, m.p. 114—115°,  $[\alpha]_D^{25}$  +42°  $\pm$  2° in MeOH, +45° in  $H_2O$ ), has been isolated from extracts of the weed together with glycerol. Possible structures for the lactone are discussed. Enzymic action of yeast, takadiastase, or emulsin affects the carbohydrate constituents of the weed without apparently affecting the activity. *d-Xylomethylonic acid phenylhydrazide*, m.p. 132—133°,  $[\alpha]_D^{25}$  +33° in MeOH, +21° in  $H_2O$ , is incidentally described. M.p. are corr. H. W.

**Preparation of lævulic acid.**—See B., 1942, II, 394.

**Formation of complex tungsto-tartrates.**—See A., 1943, I, 40.

**Long-chain acids. V. Aleuritic acid.** P. C. Mitter and S. Mukherjee (*J. Indian Chem. Soc.*, 1942, 19, 303—307).—*Et*  $\epsilon$ -bromo-, b.p. 128—130°/16 mm. (from the OH-compound and  $PBr_3$  in  $C_6H_6$ - $C_5H_5N$ ), with NaOMe yields *Et*  $\epsilon$ -methoxy-hexoate, b.p. 94—95°/15 mm., reduced (Na + EtOH) to  $\epsilon$ -methoxyhexyl alcohol, b.p. 112°/18 mm., the *bromide*, b.p. 98—99°/19 mm., from which with Mg followed by OMe $\cdot$ [CHBr] $_2$ [CH $_2$ ] $_7$ Cl (Noller *et al.*, A., 1934, 991) in Et $_2$ O yields a product converted by Zn dust in BuOH into *o*-methoxy- $\Delta^0$ -pentadecenyl chloride, b.p. 198—204°/5 mm. This yields a nitrile, hydrolysed (EtOH-KOH) to *o*-methoxy- $\Delta^0$ -hexadecenoic acid, b.p. 194°/2 mm. *Et* aleuritate is reduced (Na + BuOH) to *aleurityl alcohol*, m.p. 56°, oxidised [Pb(OAc) $_4$  in AcOH] to OH[CH $_2$ ] $_8$ CHO (small yield). A. Li.

**Production of per-acids.**—See B., 1942, II, 394.

**O-Penta-acetyl-d-gluconates of polyhydric alcohols and cellulose.** M. L. Wolfrom and P. W. Morgan (*J. Amer. Chem. Soc.*, 1942, 64, 2026—2028).—The appropriate alcohol with gluconyl chloride penta-acetate in  $C_5H_5N$  gives *ethylene glycol di-*, m.p. 94—95°,  $[\alpha] +15^\circ$ , *propane- $\alpha$ -diol di-*, m.p. 88—89°,  $[\alpha] +18.5^\circ$ , *di- $\beta$ -hydroxyethyl ether di-*, m.p. 111—112°,  $[\alpha] +12^\circ$ , *glyceryl tri-*, amorphous, softens at 58—65°,  $[\alpha] +20^\circ$ , *d-sorbitol hexa-*, amorphous, softens at 65—78°,  $[\alpha] +30^\circ$ , *d-mannitol hexa-*, amorphous, softens at 65—78°,  $[\alpha] +37^\circ$ , and  *$\alpha$ -methyl-d-glucopyranoside tetra-*, amorphous, softens at 68—72°,  $[\alpha] +57^\circ$ , *-O-penta-acetyl-d-gluconate*. In  $C_5H_5N$ , mercerised cotton linters gives a coloured, but in  $NEt_3$ - $PhNO_2$  at 80° gives a cream-coloured, *product*, containing 0.45 penta-acetyl-d-gluconyl (A) unit per anhydroglucose (B) unit. Modified cellulose acetate [1.72 Ac $^{21}$  per (B) unit],  $[\alpha]_D^{24}$  -13° in  $C_5H_5N$ , in  $C_5H_5N$  gives a *product*,  $[\alpha]_D^{21}$  -10° in  $C_5H_5N$ ,  $[\alpha]_D^{24}$  +2.5° in  $CHCl_3$  (gives dark, brittle films), containing 0.75 (A) per (B) unit, but in  $NEt_3$ - $CHCl_3$  at 60° gives a *product*,  $[\alpha]_D^{23}$  -9° in  $C_5H_5N$ ,  $[\alpha]_D^{24}$  +1° in  $CHCl_3$  (gives colourless, flexible films), containing 0.37 (A) per (B) unit. Unless otherwise stated,  $[\alpha]$  are  $[\alpha]_D^{25}$  in  $CHCl_3$ . R. S. C.

**Production of isomeric trioxymethylene.**—See B., 1942, II, 394.

**Keten acetals. X. Elimination of hydrogen bromide from acetals of  $\alpha$ -bromo-aldehydes.** *iso*Propyl- and *n*-propyl-keten diethyl acetal. S. M. McElvain, R. L. Clarke, and G. D. Jones (*J. Amer. Chem. Soc.*, 1942, 64, 1966—1969; cf. A., 1942, II, 296).— $CHR(OEt)_2$  ( $R = Pr^\beta$ , b.p. 133—136°,  $Pr^\alpha$ , b.p. 143—144°, or  $Bu^\beta$ , b.p. 156—158°) [modified prep. from  $CH(OEt)_3$  and  $MgRX$ ] with Br give  $CMe_2Br\cdot CH(OEt)_2$ , b.p. 63—64°/7 mm.,  $CH_2EtBr\cdot CH(OEt)_2$ , b.p. 82—84°/12 mm., and  $CHPr^\beta Br\cdot CH(OEt)_2$  (I), b.p. 55—56°/3 mm. (20—40%), which with 1.4N-KOBu $^\gamma$ -Bu $^\gamma$ OH give  $CH_2\cdot CMe\cdot CH(OEt)_2$  (64%), b.p. 136—137°,  $CHMe\cdot CH\cdot CH(OEt)_2$  (41%), b.p. 48—49°/21 mm., and  $CMe_2\cdot CH\cdot CH(OEt)_2$  (62%), b.p. 59—60°/16 mm., respectively. Interaction of (I) with 0.75N- or 2N-NaOEt-EtOH or 0.75N-KOBu $^\gamma$ -Bu $^\gamma$ OH at 80° is of the second order, faster with KOBu $^\gamma$ . Bu $^\beta$ CN (prep. from Bu $^\beta$ CO $\cdot$ NH $_2$  by  $P_2O_5$  at 90°, later 130°), b.p. 127—129°, gives CBu $^\beta$ (OEt) $_3$  and thence (Br- $C_5H_5N$ ) Et $_3$   $\alpha$ -bromo-orthoisovalerate (67%), b.p. 63—64°/1.3 mm., which with Na gives *isopropylketen Et $_2$  acetal* [*aa*-diethoxy- $\gamma$ -methyl- $\Delta^a$ -butene] (80%), b.p. 96—97°/100 m., 156—157°/745 mm. (structure proved by exothermic hydrolysis by very dil. HCl to Bu $^\beta$ CO $_2$ Et). Et $_3$   $\alpha$ -bromo-ortho-n-valerate, b.p. 69—70°/2 mm., and *n*-propylketen Et $_2$  acetal [*aa*-diethoxy- $\Delta^a$ -n-pentene], b.p. 107—108°/100 mm., 167—168°/737 mm. (hydrolysed to Bu $^\alpha$ CO $_2$ Et), are similarly prepared.  $CHR_2\cdot CH\cdot C(OEt)_2$  are not rearranged to  $CR_2\cdot CH\cdot CH(OEt)_2$  by boiling KOBu $^\gamma$ -Bu $^\gamma$ OH. The mode of elimination of HBr from (I) is inconclusively discussed. R. S. C.

**Manufacture of ketens and olefines.**—See B., 1942, II, 395.

**Condensation products of keten with ketones.** B. H. Gwynn with E. F. Degering (*J. Amer. Chem. Soc.*, 1942, 64, 2216—2218).—Keten reacts with ketones having  $\leq 3$   $\alpha$ -H in presence of a little  $H_2SO_4$  (not  $H_3PO_4$  or  $p$ - $C_6H_4$ Me $\cdot$ SO $_3$ H), giving enol acetates (properties described). COMe $_2$ , COMeEt, mesityl oxide, etc. react rapidly; CPhMe, COMeBu $^\gamma$ , and  $CMe_2\cdot CH\cdot COMe$  react slowly, and CPh $^\beta$  not at all. R. S. C.

**Photo-enolisation of ketones.**—See A., 1943, I, 40.

**Manufacture of (A) quaternary ammonium compounds, (B) carboxyl chlorides, and (C) carboxyl esters, of quaternary ammonium compounds.**—See B., 1942, II, 395.

**Nature and constitution of shellac. XVI. Preparation of  $\theta$ -tri-hydroxypentadecylamine from aleuritic acid by the Naegeli-Curtius series of reactions.** A. L. Davis and W. H. Gardner (*J. Amer. Chem. Soc.*, 1942, 64, 1902—1905; cf. A., 1941, II, 265).—Aleuritic [ $\theta$ -tri-hydroxypalmitic] acid, m.p. 101—101.5°, and 5% HCl-MeOH give the *Me* ester, m.p. 73°, and thence the *hydrazide*, m.p. 139—139.5°, which with aq. NaNO $_2$  and then 25% AcOH at 0° gives the azide (I), decomp. 52°. In boiling  $C_6H_6$ , (I) gives  $\theta$ -tri-hydroxypentadecylcarbimide, m.p. 103.5—104.5°, hydrolysed by boiling 50% aq. NaOH to the *amine*, m.p. 146—147° [*picrate*, m.p. 118—119° (decomp.)]. In boiling  $H_2O$ , (I) gives NN'-di- $\theta$ -tri-hydroxypentadecylcarbamide, m.p. 122.5—123°, and in boiling EtOH  $\theta$ -tri-hydroxypentadecylurethane, m.p. 78—79° (cf. Nagel, A., 1927, 447; 1931, 960), neither of which products could be hydrolysed. R. S. C.

**NN-Dimethylethylenediamine and [its] derivatives.** R. Baltzly, J. S. Buck, and W. S. Ide (*J. Amer. Chem. Soc.*, 1942, 64, 2232—2233).— $NMe_2\cdot [CH_2]_2\cdot NH_2$ , b.p. 107° (hygroscopic dihydrochloride, m.p.  $\sim 160^\circ$ ), gives the *p*-nitrobenzoate hydrochloride (I), m.p. 182.5—183.5°, hydrogenated (PtO $_2$ -EtOH-HCl here and below) to the *p*-aminobenzoate dihydrochloride, m.p. 190—191° [the derived methochloride hydrochloride, decomp.  $>230^\circ$ , is obtained from the methochloride derived from (I)]. The *p*-nitrobenzoate hydrochloride, m.p. 247—248.5°, gives  $\beta$ -*p*-aminophenylureidoethyl dimethylamine [dihydrochloride, m.p. 182—184° (decomp.)]; methochloride hydrochloride, m.p. 186°.  $\beta$ -*p*-Aminophenylacetamido- [dihydrochloride, m.p. 209.5—210.5°; methochloride hydrochloride, m.p. 155—156° (decomp.)],  $\beta$ -phenylthioureido-, m.p. 83—83.5°, and  $\beta$ -sulphanil-amido-ethyl dimethylamine [dihydrochloride, m.p. 211.5—213.5° (decomp.)] are also described. R. S. C.

**Optical configuration of glutamic acid isolated from casein hydrolysates by six procedures.** (Miss) J. C. Opsahl and L. E. Arnow (*J. Amer. Chem. Soc.*, 1942, 64, 2035—2039).—After hydrolysis of casein by boiling 20% HCl the glutamic acid (I) isolated by six different methods contains 2.5—6.2% of the *d*-form. Recoveries are recorded for hydrolysates containing added *dl*-(I); for the two best methods these are 76—89 and 82—96%. The methods used are detailed. R. S. C.

***r*- $\beta$ -Hydroxyglutamic acid.** E. Abderhalden and G. Pitschak (*Z. physiol. Chem.*, 1940, 265, 31—38).—An improved method is given for the prep. of *r*- $\beta$ -hydroxyglutamic acid (I) from casein. Acetyl-*l*-glutamic acid, m.p. 186—187°, is converted by  $CH_2N_2$  and subsequent distillation into the corresponding optically inactive *Me* $_2$  ester, b.p. 158—162°/0.1 mm., m.p. 80° (also obtained from the *dl*-acid, m.p. 176—180°), and *Me* $_2$  glutamate. *r*- $\beta$ -Hydroxyglutamic acid hydrochloride, NaOAc, AcOH, and Ac $_2$ O yield a product which when treated with  $CH_2N_2$  and then distilled affords the compound  $\begin{matrix} CH_2\cdot CH \\ CO-NH \end{matrix} > C\cdot CO_2Me$ . Methylation of (I) with  $CH_2N_2$  or MeOH-HCl is accompanied by ring-closure. *Me* $_2$  carbobenzyloxyglutamate, b.p. 211—214°/0.6—0.8 mm., and  $\beta$ -hydroxyglutamate, b.p. 208—210°/0.5 mm., carbobenzyloxy-*l*-aspartic acid, m.p. 112—115°,  $[\alpha]_D^{10}$  +13.85° in aq. NaOH (*Me* $_2$  ester, b.p. 204°/0.25 mm.), and *Me* $_2$  2 : 5-diketopiperazine-3 : 6-diacetate are incidentally described. H. W.

**Manufacture of organic amides.**—See B., 1942, II, 395.

**Preparation of [linear] polyamides.**—See B., 1942, II, 395.

**Mono- and di-substituted guanidines.** J. S. Buck, R. Baltzly, and C. W. Ferry (*J. Amer. Chem. Soc.*, 1942, 64, 2231—2232).— $NH\cdot C(SMe)\cdot NH_2\cdot H_2SO_4$  and the appropriate amine give  $\beta$ -morpholinoethyl-, m.p. 197°,  $\beta$ -diethoxyethyl-, m.p. 154°, NN-dicyclohexyl-, m.p. 195°, N-benzyl-N-methyl-, m.p. 252° (decomp.), and  $\delta$ -phenox-butyl-, m.p. 199—199.5°, -guanidine sulphate, 2B,  $H_2SO_4$ ,  $C_{10}H_7\cdot NH\cdot CH_2\cdot Ph$ , CN $\cdot$ NH $_2$ , and HCl in  $C_5H_{11}\cdot OH$  give N- $\alpha$ -naphthyl-N-benzylguanidine hydrochloride, m.p. 223—224°. *p*-OMe $\cdot C_6H_4\cdot CH_2\cdot NH_2$  (2 mols.) and CNBr (1 mol.) at 150° give NN'-di-*p*-methoxybenzylguanidine hydrochloride, m.p. 125.5—126.5°.  $\alpha$ - $C_{10}H_7\cdot NH\cdot CS\cdot NHMe$  (from  $\alpha$ - $C_{10}H_7\cdot NCS$  and  $NH_2Me$ ) with *Me* $_2$ SO and then PbO-NH $_3$  gives N- $\alpha$ -naphthyl-N'-methylguanidine hydrochloride, m.p. 220—220.5° (decomp.). R. S. C.

## II.—SUGARS AND GLUCOSIDES.

**Synthesis of epilactose and lactose.** W. T. Haskins, R. M. Hanna and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, 64, 1852—1856).—Total synthesis of epilactose and lactose is detailed (cf. A., 1942, II, 351). Condensation of acetobromo-*d*-galactose (prep. from  $\beta$ -*D*-galactopyranose penta-acetate by HBr-AcOH at 0° and later 5°), m.p. 84—85° (lit. 82—83°, 85°),  $[\alpha] +242^\circ$  in  $C_6H_6$  (cf. A., 1924, i, 371), and 2 : 3-isopropylidene-*D*-mannosan  $<1.5>\beta<1.6>$  b.p.

$\text{Ag}_2\text{O}-\text{CaSO}_4\text{-I}$  in  $\text{CHCl}_3$  at  $24^\circ$  7 days), hydrolysis of the product by 80%  $\text{AcOH}$  at  $100^\circ$ , and heating with  $\text{NaOAc}-\text{Ac}_2\text{O}$  at  $100^\circ$  gives 4- $\beta$ -D-galactopyranosido-D-mannosan  $<1.5>\beta<1.6>$  2:3:2':3':4':6'-hexa-acetate (30%), m.p.  $193-194^\circ$ ,  $[\alpha]_D^{20} -62.7^\circ$  in  $\text{CHCl}_3$ . With  $\text{H}_2\text{SO}_4-\text{Ac}_2\text{O}-\text{AcOH}$  at  $0^\circ$  this gives  $\alpha$ -epilactose octa-acetate (I) (99%), m.p.  $96-97^\circ$ ,  $[\alpha]_D^{20} +41.2^\circ$  in  $\text{CHCl}_3$ , hydrolysed by  $\text{Ba}(\text{OMe})_2-\text{MeOH}$  at  $5^\circ$  to  $\beta$ -epilactose, m.p.  $195-196^\circ$ ,  $[\alpha]_D^{20} +\sim 17^\circ \rightarrow +27.2^\circ$  in  $\text{H}_2\text{O}$  ( $k$  0.0151).  $\text{HBr}-\text{AcOH}-\text{Ac}_2\text{O}$  at  $5^\circ$  and then  $\text{Zn dust}-\text{H}_2\text{PtCl}_6$  in 50%  $\text{AcOH}$  at  $0^\circ$  converts (I) into lactal hexa-acetate, m.p.  $114^\circ$ ,  $[\alpha]_D^{20} -18.0^\circ$  in  $\text{CHCl}_3$ , which with  $\text{BzO}_2\text{H}$  in  $\text{Et}_2\text{O}-\text{EtOAc}-\text{H}_2\text{O}$  at  $25^\circ$  gives  $\beta$ -lactose hexa-acetate, m.p.  $89-90^\circ$ ,  $[\alpha]_D^{20} -4.5^\circ$  in  $\text{CHCl}_3$ , and thence  $[\text{Ba}(\text{OMe})_2]$   $\alpha$ -lactose,  $+\text{H}_2\text{O}$ , m.p.  $202^\circ$  (decomp.),  $[\alpha] +81^\circ \rightarrow +52.7^\circ$  in  $\text{H}_2\text{O}$  ( $k$  0.0042). M.p. are corr. R. S. C.

**Reactions relating to carbohydrates and polysaccharides. LXV.** Improved technique for fractionation of partly methylated glucosides. I. Levi, W. L. Hawkins, and H. Hibbert (*J. Amer. Chem. Soc.*, 1942, **64**, 1957—1959).—Small quantities of glucosides are fractionated (Podbielniak; apparatus described) with 95—97% recovery and formation of  $<1\%$  of non-volatile residue. In an example, 2.957 g. of 2:3-di-, 2:3:4-tri-, and 2:3:4:6-tetra-methylmethylglucosides are thus separated. R. S. C.

**Reactions relating to carbohydrates and polysaccharides. LXVI.** Structure of the dextran synthesised by the action of *Leuconostoc mesenteroides* on sucrose. I. Levi, W. L. Hawkins, and H. Hibbert (*J. Amer. Chem. Soc.*, 1942, **64**, 1959—1962).—The semi-micro-distillation technique (see above) is used to confirm the finding (A., 1938, II, 44; cf. Brauns, A., 1938, II, 220) that the dextran named yields, by complete methylation and hydrolysis, a 1:3:1 mixture of 2:3-di- (I), 2:3:4-tri-, and 2:3:4:6-tetra-methylmethylglucoside. (I) is identified as 2:3-dimethylglucophenylhydrazide. Possible structures for the dextran are indicated. R. S. C.

**Lichenin.** E. G. V. Percival and H. Granichstdten (*Nature*, 1942, **150**, 549).—Lichenin (I) with 1 mol. of  $\text{KOH}$  for each anhydroglucose unit forms an unstable additive compound, but both 2- and 6-methylglucose are present in the products of hydrolysis after methylation under anhyd. conditions. This indicates that the primary alcohol groups in (I) are not shielded as in cellulose. A. A. E.

**Molecular constitution of enzymically synthesised starch.** W. Z. Hassid and R. M. McCready (*J. Amer. Chem. Soc.*, 1941, **63**, 2171—2173).—Starch (I),  $[\alpha]_D +170^\circ$  in  $n\text{-NaOH}$ , synthesised from the Cori ester by potato phosphorylase, with  $\text{Ac}_2\text{O}-\text{C}_6\text{H}_5\text{N}$  at  $60^\circ$  gives a "triacetate,"  $[\alpha]_D +170^\circ$  in  $\text{CHCl}_3$ , mol. wt. ( $\eta$ ) 84,000, hydrolysed by 0.5N- $\text{KOH}$  at room temp. to (I),  $[\alpha]_D +168^\circ$ , and converted by  $\text{Me}_4\text{SO}_4\text{-}30\% \text{NaOH}$  at  $55^\circ$  into a "Me<sub>3</sub>" ether,  $[\alpha]_D +216^\circ$  in  $\text{CHCl}_3$ , mol. wt. ( $\eta$ ) 54,000. This, by hydrolysis, gives 2:3:6-tri- but no tetra- or di-methylglucose, showing that the glucose units form long chains or loops and that natural synthesis of starch involves enzymes more complicated than phosphorylase. R. S. C.

**Estimation of the dialdehyde type of oxidation in hydroxystarches and hydroxycelluloses.** D. H. Grangaard, E. K. Gladding, and C. B. Purves (*Paper Trade J.*, 1942, **115**, TAPPI Sect., 75—80).—Oxidation of starch and cellulose by  $\text{HIO}_4$  changes the glucose residues of which they consist into chains of semi-acetals of  $(\text{CHO})_2$  with 2 erythrose units. Boiling 10%  $\text{HCl}-\text{MeOH}$  converts periodate-hydroxystarch (I) into  $\sim 50\%$  of the expected amount of  $[\text{CH}(\text{OMe})_2]_2$ , isolated by means of its volatility with steam and determined as  $(\text{CHO})_2$  either colorimetrically or by pptn. with 2:4:1- $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$ . The other half of the  $(\text{CHO})_2$  residues in (I) condenses with the erythrose residues present during methanolysis to a cyclic acetal which probably contains a 1:4-dioxan ring. Control experiments show that this substance is only slightly volatile with steam and interferes in a reproducible way with the determination of  $[\text{CH}(\text{OMe})_2]_2$ . When the analytical method is extended to include both acetals it recovers  $\leq 90\%$  of the  $(\text{CHO})_2$  units present in (I) or periodate-hydroxycellulose (II). Oxidation of starch by aq.  $\text{IO}_4^-$  is selective only below  $20^\circ$  and within the limits pH 2—5 and in these conditions is 90—95% efficient. Properly prepared (II) gives analyses corresponding to  $\sim 90\%$  of dialdehydic oxidation and possibly a trace of the same type of oxidation is present in a  $\text{MnO}_4^-$ -hydroxycellulose. Entirely negative results are obtained with products formed by means of  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{OBr}^-$ ,  $\text{OCl}^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{HNO}_3$ . It is probable that the no. of different Cu-reducing structures initially produced from cellulose by any oxidising agent is  $\geq 4$ . H. W.

**Determination of the mol. wt. of cellulose by an end-group method.**—See A., 1943, I, 8.

**O-Penta-acetyl-d-gluconates of cellulose.**—See A., 1943, II, 23.

### III.—HOMOCYCLIC.

**Formation of cyclopropanes.**—See A., 1943, II, 21.

**Isomerisation of  $\beta$ -carotene.** Isolation of a stereoisomeride having increased adsorption affinity. A. Polgr and L. Zechmeister

(*J. Amer. Chem. Soc.*, 1942, **64**, 1856—1861).— $\beta$ -Carotene (I) is converted by heat (boiling light petroleum, b.p.  $60-70^\circ$ ;  $190^\circ$ ) ( $\text{CO}_2$ ) or catalysts (I- or conc.  $\text{HCl}$ -light petroleum) into a mixture of pigments, of which 9—10 are stereoisomerides of (I). The products are separated by chromatography  $[\text{Ca}(\text{OH})_2]$ . The isolated products are isomerised by I to similar mixtures containing much (I). Some of the products are adsorbed more strongly than is (I). Of these, *neo*- $\beta$ -carotene U (II) (17%) is obtained having m.p.  $122-123^\circ$  (corr.; block;  $\text{CO}_2$ ),  $\alpha$  0 in  $\text{C}_8\text{H}_8$ , absorption max. 4—8  $\mu$ .  $<$  those of (I). The stereochemistry is discussed. (I) probably has 1, Gillam's  $\psi$ - $\alpha$ -carotene 2, and a labile isomeride (shift of absorption max. 20  $\mu$ .) 4—5 *cis*-linkings. R. S. C.

**Methylation of aromatic nitro-compounds with lead tetra-acetate.** L. F. Fieser, R. C. Clapp, and W. H. Daudt (*J. Amer. Chem. Soc.*, 1942, **64**, 2052—2060).—1:2:4:6- $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$  (I) is methylated by  $\text{Pb}(\text{OAc})_4$  in  $\text{AcOH}$  to 1:3:2:4:6- $\text{C}_6\text{HMe}_2(\text{NO}_2)_3$  (II), interaction being induced by long heating at  $100^\circ$ , boiling for a short time, local superheating, or adding  $\text{CH}_2(\text{CO}_2\text{H})_2$ . Yields are the same by all methods, but optimum (28—32%) if 2.5—3 equivs. of  $\text{Pb}(\text{OAc})_4$  are used. Methylation is also effected by warm  $\text{Pb}_2\text{O}_3\text{-AcOH}$  or by prolonged boiling with  $\text{PbO}_2\text{-AcOH}$ . *s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$  gives similarly (I) + some (II), but (II) is unaffected by further treatment. *m*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$  gives  $\sim 30\%$  of 1:2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$  + 1:3:4:6- or 1:3:2:4- $\text{C}_6\text{H}_2\text{Me}_2(\text{NO}_2)_2$ ; for identification the products are nitrated, the (II) formed is separated, and (I) then isolated as complex with  $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ .  $\text{PhNO}_2$  with  $\text{Pb}(\text{OAc})_4$  (3 mols.) gives 4.9% of *o*- + some *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ , isolated by nitration etc. as above and converted by fractionation and subsequent oxidation into *o*- + *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ . After a long induction period, 2.4 equivs. of  $\text{Pb}(\text{OAc})_4$  are consumed by boiling  $\text{C}_6\text{H}_6\text{-AcOH}$ , but the product (18%) is  $\text{CH}_2\text{Ph}\cdot\text{OAc}$ ; methylation is the first reaction, since  $\text{PhMe}$  and  $\text{Pb}(\text{OAc})_4$  give  $\text{CH}_2\text{Ph}\cdot\text{OAc}$  (11%).  $\text{PhCl}$  similarly gives (? mixed)  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot\text{OAc}$ , whence alkali yields *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ .  $\text{C}_{10}\text{H}_8$  is oxidised, yielding  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OAc}$  (26%). Trials with  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NO}_2$ , 1:5- and 1:8- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$ , 1:3:8- and 1:4:5- $\text{C}_{10}\text{H}_5(\text{NO}_2)_3$ , and 1:3:6:8- $\text{C}_{10}\text{H}_4(\text{NO}_2)_4$  are unpromising, but a trace of 2:1:8- $\text{C}_{10}\text{H}_5\text{Me}(\text{NO}_2)_2$  is obtained. (II) is obtained from (I) by  $\text{Ac}_2\text{O}_2$  in boiling  $\text{C}_6\text{H}_6$  (10.6%) or by anodic oxidation in  $\text{NaOAc}-\text{AcOH}$  (9% yield), which reactions suggest possible mechanisms. R. S. C.

**Kinetics of the oxidation by permanganate of side-chains to the benzene nucleus. I. Oxidation of monochlorotoluenes.**—See A., 1943, I, 38.

**Preparation of benzene derivatives [diphenyls].**—See B., 1942, II, 395.

**Further nitration of dinitrodiphenyls.** F. H. Case (*J. Amer. Chem. Soc.*, 1942, **64**, 2225).—Hot  $\text{HNO}_3$  (*d* 1.5) converts 2:3'-di- into 2:4:3'-tri-nitrodiphenyl, m.p.  $137-138^\circ$  (cf. Blakey *et al.*, A., 1928, 165), also obtained similarly with the 3:4:4'-( $\text{NO}_2$ )<sub>3</sub>-derivative, m.p.  $205-206^\circ$ , from the 3:4'-( $\text{NO}_2$ )<sub>2</sub>-compound (proof of structure). (*m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4$ )<sub>2</sub> gives 3:4:3'-trinitrodiphenyl, m.p.  $179-180^\circ$ , which yields the known 3:3:3':4'-( $\text{NO}_2$ )<sub>4</sub>-derivative, m.p.  $203-204^\circ$  (lit.  $186^\circ$ ). R. S. C.

**Nitration of halogenodiphenyls. I. Nitro-derivatives of 4-bromo-diphenyl.** F. H. Case (*J. Amer. Chem. Soc.*, 1942, **64**, 1848—1852).—Nitration of *p*- $\text{C}_6\text{H}_4\text{PhBr}$  gives 4-bromo-3:4'-(I), m.p.  $210-211^\circ$  (lit.  $205-206^\circ$ ), and -3:4'-dinitrodiphenyl (II), m.p.  $154-155^\circ$  (lit.  $147-148^\circ$ ) (cf. A., 1927, 1062; 1934, 62; 1938, II, 225), structures being proved thus. (I) is obtained from 3:4- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot 4'$  by, successively,  $\text{NaNO}_2$ -conc.  $\text{H}_2\text{SO}_4$  at  $0^\circ$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{Br}-\text{NaBr}-\text{H}_2\text{O}$  at  $0^\circ$ , and  $\text{Cu}$ , and by nitration of 4- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{Br}-4'$  (III). (II) is obtained from 2- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{Br}-4'$  (IV) by conc.  $\text{HNO}_3\text{-H}_2\text{SO}_4$  at  $<30^\circ$  and with  $\text{CrO}_3$  gives 3:4:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}_2\text{H}$  (V). 4-Bromo-3:2':4'-trinitrodiphenyl, m.p.  $180-181^\circ$ , is obtained from (I), (II), (III), or (IV) by  $\text{HNO}_3$  (*d* 1.59) at  $100^\circ$  (cf. Le Fvre *et al.*, A., 1926, 1027). Nitration of 3- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{Br}-4'$  gives, according to the conditions, (a) a mixture (VI),  $\text{C}_{12}\text{H}_6\text{O}_6\text{N}_3\text{Br}$ , m.p.  $181-182^\circ$  [oxidised to (V)], and a little 4-bromo-2:3'-dinitrodiphenyl (VII), m.p.  $143-144^\circ$ , (b) (VII) and 4-bromo-3:3'-dinitrodiphenyl (VIII), m.p.  $189-190^\circ$  [oxidised to (V)], or (c), by  $\text{HNO}_3$  (*d* 1.59) at  $100^\circ$ , 4-bromo-2:3':4'-(IX), m.p.  $170-171^\circ$ , and a little 4-bromo-3:3':4'-tri-nitrodiphenyl, m.p.  $192-193^\circ$  [obtained similarly from (VI)]. 3- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot 4'$  and  $\text{KNO}_3$ -oleum at  $<6^\circ$  give 2:3'-dinitro-4-aminodiphenyl, m.p.  $157-158^\circ$  (*Ac* derivatives, m.p.  $215-216^\circ$ ), and thence 2- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot 3'$  and (VII). 3- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}\cdot 4'$  and  $\text{HNO}_3$  (*d* 1.5) in  $\text{Ac}_2\text{O}-\text{AcOH}$  give 3:3'-dinitro-4-aminodiphenyl, m.p.  $206-207^\circ$ , by way of the *Ac* derivative (X), m.p.  $241-242^\circ$ , and thence (3- $\text{NO}_2\cdot\text{C}_6\text{H}_4$ )<sub>2</sub> and (VIII). With  $\text{NH}_3\text{-EtOH}$  at  $150^\circ$  (IX) gives 4-bromo-2:3'-dinitro-4-aminodiphenyl, m.p.  $223-224^\circ$ , and thence (VII) and 2:4- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{NO}_2\cdot 4':3'$ . 3:4-Dinitrodiphenyl [prep. from 1:3:4- $\text{C}_6\text{H}_3\text{I}(\text{NO}_2)_2$ ,  $\text{PhI}$ , and  $\text{Cu}$  powder at  $280^\circ$ ], m.p.  $87-88^\circ$ , with  $\text{NH}_3\text{-EtOH}$  at  $150^\circ$  gives 3:1:4- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Ph}\cdot\text{NH}_2$  and with  $\text{Br}-\text{AcOH}-\text{FeCl}_3$  (trace) at  $90^\circ$  gives 4-bromo-3':4'-dinitrodiphenyl (XI), m.p.  $167-168^\circ$ , converted by  $\text{HNO}_3$  (*d* 1.59) into 4-bromo-

3:3':4'-trinitrodiphenyl, m.p. 192—193°, which is also obtained from (VI) or (XI).  $\text{HNO}_3$  (*d* 1.5) at <8° converts 3:4:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NHAc})\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot 3'$  into 3:5:3'-trinitro-4-acetamido-, m.p. 242—243° (also obtained from 3- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}\cdot 4'$ ), and thence 4-amino-diphenyl, m.p. 233°. With, successively,  $\text{NaNO}_2\text{--H}_2\text{SO}_4$  at 0°,  $\text{H}_3\text{PO}_4$  at 2°, oleum at 15—20°, and boiling EtOH, (X) gives 3:5:3'-trinitrodiphenyl, m.p. 177—178° [also obtained from  $m\text{-C}_6\text{H}_4\cdot\text{I}\cdot\text{NO}_2$ , 1:3:5- $\text{C}_6\text{H}_3\text{I}(\text{NO}_2)_2$  (XII), and Cu powder at 270°], and by Schoutissen's method 4-bromo-3:5:3'-trinitrodiphenyl, m.p. 222—223°. 3:5:3':5'-Tetranitrodiphenyl, m.p. 228—229°, is obtained from (XII) by Cu powder at 270°.

R. S. C.

**Preparation of polycyclohexyldiphenyls.**—See B., 1942, II, 396.

**Separation of *cis*- and *trans*-stilbenes by application of the chromatographic brush method.** L. Zechmeister and W. H. McNeely (*J. Amer. Chem. Soc.*, 1942, **64**, 1919—1921).—*cis*- and *trans*-(CHPh) $_2$ , *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{CH}:\text{CHPh}$ , and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}:\text{CHPh}$  are separated by adsorption on  $\text{Al}_2\text{O}_3$ , extruding the column, and painting a streak with 1%  $\text{KMnO}_4$  down the column; the two zones are indicated by brown stains. 1—2% of one form can be detected in the other.

R. S. C.

**"Tervalent" carbon. XXI. Tetracyclohexyldiphenylethane.** K. Ziegler and P. Herte (*Annalen*, 1942, **551**, 222—234; cf. Marvel *et al.*, A., 1930, 1279; Neunhoeffer, A., 1937, II, 16).—Dicyclohexylphenylcarbinol is converted by AcOH saturated with HBr in Et $_2$ O into the bromide, m.p. 126—127°, which with dry  $\text{Ag}_2\text{O}$  and powdered  $\text{AgNO}_3$  in MeOH affords dicyclohexylphenylmethyl Me ether, m.p. 75—76°. This is transformed by K—Na into the corresponding K compound (I), converted by EtOH into dicyclohexylphenylmethane, b.p. 201—202°/12 mm. (*p*- $\text{NO}_2$ -derivative, m.p. 112—113°), also obtained by hydrogenation of cyclohexylcyclohexylidenephenylmethane, and by  $\text{CO}_2$  into dicyclohexylphenylacetic acid (II), m.p. 250—252° (lit. 242—244°) (*Ag* salt). (I) and  $(\text{CMe}_2\text{Br})_2$  in Et $_2$ O at -15° to -20° afford tetracyclohexyldiphenylethane, m.p. 157—158° (under  $\text{N}_2$ ), transformed by K—Na followed by  $\text{CO}_2$  into (II). The mol. wt. in freezing  $\text{C}_6\text{H}_6$  is 470. It is autoxidised in boiling Et $_2$ O to dicyclohexylphenylmethyl peroxide, m.p. 182—184°; in presence of pyrogallol (III) it appears to yield the H peroxide which has not been definitely characterised. Its rate of autoxidation resembles that of any other labile ethane and in particular the rate of absorption of  $\text{O}_2$  is independent of the  $\text{O}_2$  pressure if (III) is present. In  $\text{C}_6\text{H}_6$  it decolorises I but the reaction cannot be regarded as an identification of radicals since the rate of decomp. at room temp. is too small to permit a sufficiently rapid addition of I, which obviously attacks directly the very weak, central C—C linking. It greatly accelerates the autoxidation of  $\Delta^1:3$ -cyclohexadiene and styrene. Solutions of the substance in  $\text{C}_6\text{H}_6$ , prepared with exclusion of air, lose their ability as  $\text{O}_2$ -carriers after prolonged heating, the ethane being irreversibly decomposed after primary dissociation followed by disproportionation.

H. W.

**Dissociation of hexa-arylethanes. XIV. Ethanes derived from mixtures of triaryl halides.** C. S. Marvel and C. M. Himel (*J. Amer. Chem. Soc.*, 1942, **64**, 2227).—Treating mixed triarylmethyl halides (6 pairs) with Ag gives products, the degree of dissociation of which (determined by magnetic susceptibility) is  $\ll$  the mean of the dissociation of the pairs of radicals.

R. S. C.

**Dissociation of hexa-arylethanes. XII. Effect of naphthyl and diphenyl groups.** C. S. Marvel, J. W. Shackleton, C. M. Himel, and J. Whitson (*J. Amer. Chem. Soc.*, 1942, **64**, 1824—1825; cf. A., 1941, II, 284).—The following % dissociation in 0.1M. solution in  $\text{C}_6\text{H}_6$  are determined by means of magnetic susceptibilities: [ $(p\text{-C}_6\text{H}_4\text{Ph})_2\text{CPh}$ ] $_2$   $18\pm 2$ , ( $p\text{-C}_6\text{H}_4\text{Ph}$ ) $_6\text{C}_2$   $26\pm 5$ , ( $\beta\text{-C}_{10}\text{H}_7\cdot\text{CPh}$ ) $_2$   $6\pm 2$ , [ $(\beta\text{-C}_{10}\text{H}_7)_2\text{CPh}$ ] $_2$   $13\pm 2$ , ( $\beta\text{-C}_{10}\text{H}_7$ ) $_6\text{C}_2$   $21\pm 10$ ,  $24\pm 5$ , ( $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\text{Ph}\cdot p$ ) $_2$   $54\pm 2$ . The relatively low results of Bachmann *et al.* (A., 1937, II, 90) are thus confirmed. Calculation for 0.1M. solution by the law of mass action from measurements at other concns. is proved permissible ( $26\pm 2$  to  $29\pm 5$ ) for 0.839—7.0% solutions of ( $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CPh}$ ) $_2$  in  $\text{C}_6\text{H}_6$  at 25°.  $\beta\text{-C}_{10}\text{H}_7$  are much less dissociated than are  $\alpha\text{-C}_{10}\text{H}_7$  derivatives. Phenyl-di- $\beta$ -naphthyl-, m.p. 168—169°, and *p*-diphenylmethyl peroxide, m.p. 151—152°, and phenyl-di- $\beta$ -naphthylmethyl chloride, m.p. 159—160°, are described.

R. S. C.

**Quaternary salts.** R. Baltzly, C. W. Ferry, and J. S. Buck (*J. Amer. Chem. Soc.*, 1942, **64**, 2231).— $n\text{-C}_{18}\text{H}_{37}\cdot\text{NPhMe}$ , b.p. 234°/3 mm. (methiodide, m.p. 93—94°),  $\beta$ -cyclohexylethylbenzyltrimethylammonium chloride, m.p. 206° (decomp.), benzyltrimethyl- $\beta$ -bromoethylammonium bromide, m.p. 174°, and  $\alpha$ -naphthylmethyltriethylammonium chloride, m.p. 197° (decomp.), are prepared.

R. S. C.

**Acylacetarlamides.**—See B., 1943, II, 5.

**Influence of the 5-nitro-group on halogenation and nitration of 5-nitro-1-naphthylamine and related naphthalides.** H. H. Hodgson and H. S. Turner (*J.C.S.*, 1942, 723—725).—5:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$  (I) yields with Br in  $\text{CHCl}_3$  at 50° 2-bromo-, m.p. 121.5° (*Ac* derivative, m.p. 139°) [deaminated by diazotisation ( $\text{NaNO}_2\text{--H}_2\text{SO}_4$  in AcOH) and treatment with  $\text{Cu}_2\text{O}$  in EtOH to 2:5- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NO}_2$ ],

or 2:4-dibromo-5-nitro-1-naphthylamine, m.p. 159.5° [*Ac* derivative, m.p. 230.5° (decomp.)], and with  $\text{Hg}(\text{OAc})_2$  in AcOH at 100°, 5-nitro-1-naphthylamine-2-mercuriacetate, m.p. >400°. This with I in aq. KI at 100° gives 2-iodo-5-nitro-1-naphthylamine, m.p. 121.5—122.5° (*Ac* derivative, m.p. 169.5°), converted (diazo-methods) into 2:5- $\text{C}_{10}\text{H}_6\text{I}\cdot\text{NO}_2$ , new m.p. 91.5°, and 1:2-di-iodo-5-nitronaphthalene, m.p. 132.5°. 5:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NHAc}$  (II) with  $\text{Cl}_2$  in AcOH at 100° yields only the *Ac* derivative, m.p. 235.5°, of 2:4-dichloro-5-nitro-1-naphthylamine, m.p. 116.5°, deaminated (as above) to 2:4-dichloro-5-nitronaphthalene, m.p. 116.5°. Nitration of (II) gives 4:5:1-( $\text{NO}_2$ ) $_2\text{C}_{10}\text{H}_5\cdot\text{NHAc}$ , hydrolysed and deaminated to 1:8- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$ . 5-Nitro-*p*-toluenesulphon-1-naphthalide, m.p. 171° [from (I) and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  in  $\text{C}_6\text{H}_5\text{N}$ ], and AcOH- $\text{HNO}_3$  (*d* 1.5) yield the  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$  derivative, m.p. 206°, of 2:4:5:1-( $\text{NO}_2$ ) $_3\text{C}_{10}\text{H}_4\cdot\text{NH}_2$ , m.p. 310° (lit. 305°, 310°). 2-Chloro-5-nitronaphthalene (from 5:2- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ ) has m.p. 100.5°.

A. Li.

**Phenylthiocarbamides. The triad -N·C·S-. XII. Phenylcyanamide, its properties and derivatives.** Phenylhydrazine- $\alpha$ -carboxylic acid. R. Sahasrabudhey and H. Krall (*J. Indian Chem. Soc.*, 1942, **19**, 343—348).— $\text{NHPH}\cdot\text{CS}\cdot\text{NH}_2$  with  $\text{Cu}(\text{OAc})_2$  in an alkaline medium gives  $\text{NHPH}\cdot\text{CN}$  [separates from  $\text{H}_2\text{O}$  as (mainly) a monohydrate at 30° and trihydrate at 0—15°; hydrochloride, m.p. 118°; H sulphate; *NO*-derivative, m.p. 155—156°, which with NaOH affords  $\text{NO}\cdot\text{NPH}\cdot\text{CO}_2\text{Na}$  (corresponding *Ag* salt), reduced (Sn, dil. HCl) to  $\text{CO}_2\text{H}\cdot\text{NPH}\cdot\text{NH}_2\cdot\text{HCl}$ ].  $\text{NHPH}\cdot\text{CN}$  polymerises to triphenylisomelamine.

F. R. S.

**Preparation of sulphanilylcarbamide.** E. H. Cox (*J. Amer. Chem. Soc.*, 1942, **64**, 2225—2226).— $\text{NH}_2\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{HCl}$ , *p*- $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ , and  $\text{K}_2\text{CO}_3$  in  $\text{COMe}_2\text{--H}_2\text{O}$  at 0° give *p*-acetamidobenzenesulphonyl-*O*-ethylisocarbamide (87%), m.p. 223—224°, hydrolysed by conc. HCl at 100° to sulphanilylcarbamide (80%), m.p. 140—146° (gas) ( $\text{NH}_4$ , *K*, and *Na* salts).

R. S. C.

***p*-Aminobenzenesulphon- $\beta\beta$ -dimethylacrylamide.**—See B., 1943, III, 21.

**Acylation experiments with sulphanilamide and heterocyclic amines. II, III.** F. Bergmann and D. Schapiro (*J. Org. Chem.*, 1942, **7**, 419—423).—Sulphanilamide (I) and  $(\text{CH}\cdot\text{CO})_2\text{O}$  in  $\text{COMe}_2$ , dioxan, or xylene give *N* $^4$ -sulphanilamidomaleic acid, m.p. 209—210°, converted by boiling 2%  $\text{H}_2\text{SO}_4\text{--EtOH}$  into the *Et* ester, m.p. 204—205°, with some *N*-phenylmaleimide-*p*-sulphonamide, softens at 220°, decomp. 285°. *trans*- $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CH}\cdot\text{COCl}$  (II) and (I) in  $\text{COMe}_2\text{--C}_6\text{H}_5\text{N}$  yield *Et N* $^4$ -sulphanilamidofumarate, m.p. 219° (corresponding *acid*, m.p. 295°). (I) and citraconic anhydride in dioxan at 5° and then at room temp. afford the *acid*,  $\text{C}_{11}\text{H}_{12}\text{O}_5\text{N}_2\text{S}$ , m.p. 175° and  $\sim 210^\circ$  after re-solidification, easily transformed into the *imide*, m.p. 217—218°. 8-Amino-6-methoxyquinoline (III) and  $(\text{CH}\cdot\text{CO})_2\text{O}$  in boiling  $\text{COMe}_2$  yield 6-methoxyquinoline-8-*N*-maleamic acid, m.p. 225° [*Et* ester, m.p. 177°, and its hydrochloride (+0.5 $\text{H}_2\text{O}$ ), m.p. 212° (decomp.)]. *Et* 6-methoxyquinoline-8-*N*-fumaramate, m.p. 105° [hydrochloride, m.p. 195° (decomp.)], results from (II) and (III) in  $\text{COMe}_2$ . 6-Methoxyquinoline-8-citraconimide has m.p. 179°.

III. Gradual addition of  $\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{COCl}$  in  $\text{C}_6\text{H}_6$  to (III) in  $\text{C}_6\text{H}_6$  leads to 8- $\beta$ -chloropropionamido-6-methoxyquinoline, m.p. 104°, which with boiling  $\text{MeOH--NHET}_2$  gives  $\gamma$ -acrylamido-6-methoxyquinoline, b.p. 210°/0.4 mm., m.p. 119—120° (hydrochloride, m.p. 208°; dibromide, m.p. 171—172°).

H. W.

**Interpretation of the Sandmeyer reaction. III. Further evidence in favour of a mechanism involving anionoid halogen.** H. H. Hodgson, S. Birtwell, and J. Walker (*J.C.S.*, 1942, 720—723).— $\text{PhN}_2\text{HSO}_4$  with  $\text{CuSO}_4$  and NaBr gives 38% of PhBr. The yield (63%) of  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$  (I) from  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{HSO}_4$ ,  $\text{CuSO}_4$ , and NaBr is unaffected by added  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , but  $\text{FeCl}_3$  gives 74% of a 1:1 mixture of (I) and  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$  (II); with  $\text{H}_2\text{O}_2$  the yield of (I) is reduced. Conversion of  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  into (II) is catalysed by  $\text{FeCl}_3$  or  $\text{CuCl}_2$  in  $\text{H}_2\text{O}$  or in HCl but not by  $\text{ZnCl}_2$ ;  $\text{SnCl}_4$  and  $\text{AlCl}_3$  have little effect. Production of ArCl from  $\text{ArN}_2\text{Cl}$  and  $\text{CuCl}_2$  (or  $\text{CuSO}_4$  and NaCl) increases with increasing positivity of the diazonium cation. The reactions studied can be interpreted by the mechanism previously proposed (A., 1942, II, 52, 254).  $\text{Cu}^{\text{I}}$  salts do not possess the almost unique character claimed by Sandmeyer and by Waters (A., 1942, II, 222).

A. Li.

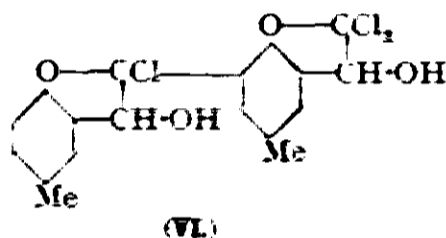
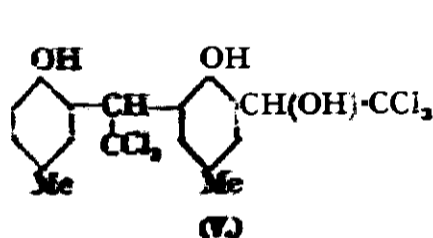
**Halogenation of esters in the diphenyl series. I. Chlorination of *p*-diphenyl acetate.** C. M. S. Savoy and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1942, **64**, 2219—2221).— $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{OAc}$  with  $\text{Cl}_2$  and a little I in  $\text{CCl}_4$  and then  $\text{KOH--aq. EtOH}$  gives 4-chloro-4'-hydroxydiphenyl, m.p. 145—146° (acetate, m.p. 113°), also obtained (4%) by treating benzidine with, successively,  $\text{NaNO}_2\text{--aq. HCl}$ ,  $\text{CuCl--HCl}$  at room temp. and later 60°, and  $\text{NaNO}_2\text{--aq. HCl}$  at room temp. and later 60°. 2-Chloro-, m.p. 68°, 2:6-dichloro-, m.p. 64°, and 2:6:4'-trichloro-4-diphenyl acetate, m.p. 79.5°, are prepared from the corresponding phenols by boiling  $\text{NaOAc--Ac}_2\text{O}$ .

R. S. C.

**Nuclear methylation of phenols by means of methanolic sodium methoxide.** J. W. Cornforth, (Mrs.) R. H. Cornforth, and (Sir) R. Robinson (*J.C.S.*, 1942, 682—684).—The C-methylation method

used in the pyrrole series is extended. Although PhOH, *o*- and *p*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> and *m*-C<sub>6</sub>H<sub>3</sub>(OH)<sub>2</sub> are unaffected by NaOMe-MeOH at 220° (autoclave) for ~10 hr., β-C<sub>6</sub>H<sub>3</sub>(OH) (I) is partly methylated to 1:2-C<sub>6</sub>H<sub>3</sub>Me-OH (II). Resorcinol (III) and *s*-C<sub>6</sub>H<sub>3</sub>(OH)<sub>2</sub> similarly yield 2:4:6:1:3-C<sub>6</sub>HMe<sub>2</sub>(OH)<sub>2</sub>; with (III), some HCO<sub>2</sub>H and (probably) a *C*-methyl- or -dimethyl-β-resorcylic acid are also formed. 2:2'-Dihydroxy-di-*a*-naphthylmethane gives an improved yield (75%) of (II), showing that nascent (I) is more readily methylated than ordinary (I). Benzylidenedi-β-naphthol gives 2:1-OH-C<sub>10</sub>H<sub>7</sub>-CH<sub>2</sub>Ph, (I) and (II), whilst 1-piperidino-2- and 4-piperidino-1-naphthol yield (II) [(I) is not formed] and 4:1-C<sub>10</sub>H<sub>7</sub>Me-OH, respectively. 2:7-Dihydroxy-1:8-bis(piperidino-methyl)phenanthrene, m.p. 219–220° (from 2:7-dihydroxyphenanthrene, piperidine, and aq. CH<sub>3</sub>O in EtOH), is reduced by NaOMe-MeOH at 200° for 6 hr., and the product methylated to (probably) 2:7-dimethoxy-1:8-dimethylphenanthrene, m.p. 256–257°. Mechanisms of reaction are discussed. A. T. P.

Interaction of *p*-cresol and other phenols with chloral and its hydrate. M. P. Balfe and W. C. Webber (J.C.S., 1942, 718–720).—In CHCl<sub>3</sub> at room temp. in presence of K<sub>2</sub>CO<sub>3</sub>, CCl<sub>3</sub>-CHO yields with PhOH, Ph (7.5%), m.p. 15–18°, and with *p*-cresol, *p*-tolyl 3:3:3-trichloro-*a*-hydroxyethyl ether (35%) (I), m.p. 46–47°, but does not react with *o*- or *m*-cresol, *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-OH, or *p*-OH-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>H. Repeated saturation of molten *p*-cresol + CCl<sub>3</sub>-CH(OH)<sub>2</sub> with HCl yields 3:3:3-trichloro-*a*-hydroxyethyl-*p*-cresol (35%) (II), also obtained when (I) is kept for several months in HCl gas or in solution containing K<sub>2</sub>CO<sub>3</sub>. (II) in AcOH saturated with HCl gives the 4-monoacetate (III), m.p. 163° [colour (fugitive when heated) with FeCl<sub>3</sub>], which with *p*-cresol and 99% H<sub>2</sub>SO<sub>4</sub> in AcOH yields the monoacetate (IV), m.p. 193°, of *aaa*-trichloro-3:3-di-4-hydroxy-*m*-tolylethane (acetate) (Ac<sub>2</sub>O-NaOAc), m.p. 162°. (II), *p*-cresol, and 99% H<sub>2</sub>SO<sub>4</sub> in AcOH at 50–60° yield (III) (IV), and a diacetate, m.p. 200° (slight decomp.) [also obtained from (II) and 99% H<sub>2</sub>SO<sub>4</sub> in PhNO<sub>2</sub> at 15°, with or without *p*-cresol; acetylated (NaOAc-Ac<sub>2</sub>O) to the triacetate, m.p. 178° of (V). (II) with aq. KOH yields the compound (VI), m.p. 184° (diacetate, m.p. 133°).



CCl<sub>3</sub>-CHO or its hydrate with (best 79.8% H<sub>2</sub>SO<sub>4</sub> yields a complex of composition CCl<sub>3</sub>-CH(OH)-O-SO<sub>2</sub>-OH·1.5H<sub>2</sub>O + 21.2% of H<sub>2</sub>SO<sub>4</sub>·1.5H<sub>2</sub>O. A. Li.

Oxidation of *p*-cresol by peroxidase. W. W. Westerfeld and C. Lowe (J. Biol. Chem., 1942, 145, 463–470).—Horseradish peroxidase, H<sub>2</sub>O<sub>2</sub>, and *p*-cresol at pH 6.5 (PO<sub>4</sub> buffer) give the ketodimethyltetrahydrodiphenylene oxide (I) of Pummerer *et al.* (A., 1925, i, 1262), 2:2'-dihydroxy-5:5'-dimethylklyphenyl (diacetate, m.p. 88°), and (probably) 2:2'-dihydroxy-3-(6'-hydroxy-*m*-tolyl)-5:5'-dimethylklyphenyl, m.p. 196–5° (triacetate, m.p. 107°) (cf. *loc. cit.*). 2:3'-Dihydroxy-5:6'-dimethylklyphenyl [from (I) and 48% HBr at 100° (bath)] (dibenzoate, m.p. 131.5–132°), is methylated (Me<sub>2</sub>SO<sub>4</sub>, 10% NaOH) and then oxidised (KMnO<sub>4</sub>, 1% NaOH) to 2:3'-dimethoxydiphenyl-3:6'-dicarboxylic acid, m.p. 263–264°. Oxidation (KMnO<sub>4</sub>, COMe<sub>2</sub>) of (I) gives 1:4-dimethyl-1:2-dihydrocoumarone-1-carboxylic-2-acetic acid (II), m.p. 149–150° (anhydride, m.p. 125–126°), oxidised (KMnO<sub>4</sub>, dil. NaOH) to 1-methyl-1:2-dihydrocoumarone-1:4-dicarboxylic-2-acetic acid, m.p. 238–240°. KOH-fusion of (II) at 250° followed by methylation (Me<sub>2</sub>SO<sub>4</sub>) and oxidation (KMnO<sub>4</sub>, 2% NaOH), gives 4:1:3-OMe-C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>H)<sub>2</sub>. P. G. M.

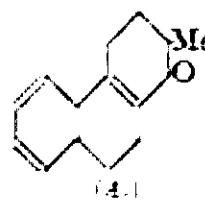
*n*-Decylresorcinol.—See B., 1943, II, 5.

Alkylquinols and related compounds. A. H. Cook, I. M. Heilbron, and F. B. Lewis (J.C.S., 1942, 659–661).—Neither *p*-anisyl stearate, m.p. 50°, nor palmitate, m.p. 51.5°, obtained from the acyl chloride and *p*-OH-C<sub>6</sub>H<sub>4</sub>-OMe-Et<sub>2</sub>O-C<sub>6</sub>H<sub>4</sub>N (cold), would undergo the Fries reaction. The following are prepared from quinol Me<sub>2</sub> or Et<sub>2</sub> ether, the acid chloride, and AlCl<sub>3</sub> in C<sub>6</sub>H<sub>5</sub>Cl<sub>2</sub> at 0°: 2:5-dimethoxy-stearophenone, m.p. 46°, -palmitophenone (I), b.p. 205°/0.18 mm., m.p. 51.5°, -myristophenone, b.p. 209°/0.5 mm., m.p. 43°, and -arophenone, b.p. 175–178°/0.2 mm., m.p. 27.5°; 2:5-diethoxy-myristophenone, b.p. 204°/0.29 mm., m.p. 44.5° (2:4-dinitrophenylhydrazones, m.p. 75°), and -laurophenone, b.p. 180–190°/0.34 mm. (2:4-dinitrophenylhydrazones, m.p. 77.5°). 2:5-Diethoxypalmitophenone-2:4-dinitrophenylhydrazone has m.p. 75°. 2:4:5-Triethoxylaurophenone melts at 53°. Clemmensen reduction affords 2:5-dimethoxy-, b.p. 188°/0.2 mm., and -diethoxy-octadecyl-, b.p. 210°/0.06 mm., 2:5-dimethoxy-, b.p. 210°/0.5 mm., and -diethoxy-hexadecyl-, b.p. 219°/0.1 mm., 2:5-dimethoxy-, b.p. 165°/0.5 mm., and -diethoxy-tetradecyl-, b.p. 183°/0.1 mm., and 2:5-dimethoxy-, b.p. 154°/0.5 mm., and -diethoxy-dodecyl-benzene, b.p. 176°/0.7 mm., dealkylated by 50% HBr-AcOH (4–6 hr.) to octadecyl-, m.p. 100.5°,

hexadecyl-, m.p. 112°, tetradecyl-, m.p. 110°, and dodecyl-quinol, m.p. 105°, which are oxidised by Ag<sub>2</sub>O-Et<sub>2</sub>O to the respective benzoquinones, m.p. 76°, 83°, 77.5°, and 72°. Octadecylbenzoquinone and Ac<sub>2</sub>O (+H<sub>2</sub>SO<sub>4</sub>) yield 2:4:5-triacetoxyoctadecylbenzene, m.p. 73°. (I) and Al(OPr<sup>i</sup>)<sub>3</sub>-Pr<sup>i</sup>OH give *a*-hydroxy-*a*-2:5-dimethoxyphenyl-hexadecane, m.p. 34°, dehydrated (NaHSO<sub>4</sub> at 200°) to *a*-2:5-dimethoxyphenyl-Δ<sup>6</sup>-hexadecene, m.p. 43°. The 2:5:1-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>-COAlk and MgMeI afford, not *tert*-alcohols, but olefines, viz., *a*-2:5-dimethoxyphenyl-*a*-methyl-Δ<sup>6</sup>-octadecene, b.p. 202°/0.5 mm., -Δ<sup>6</sup>-hexadecene, m.p. 35°, and -Δ<sup>6</sup>-tetradecene, b.p. 175°/0.2 mm., and *a*-2:4:5-trimethoxyphenyl-*a*-methyl-Δ<sup>6</sup>-dodecene, b.p. 203°/0.5 mm.; demethylation by HBr-AcOH gives 5-methoxy-2-tetradecylcoumaran (or 6-methoxy-2-tridecylchroman), b.p. 196°/0.2 mm., 5-hydroxy-3-methyl-2-hexadecylcoumaran (or 6-hydroxy-4-methyl-2-pentadecylchroman), b.p. 192–194°/0.2 mm., 5-hydroxy-3-methyl-2-tetradecylcoumaran (or 6-hydroxy-4-methyl-2-tridecylchroman), b.p. 200°/0.2 mm., and 5-hydroxy-3-methyl-2-decylcoumaran (or 6-hydroxy-4-methyl-2-nonylchroman), b.p. 178–183°/0.2 mm. Palmityl-*o*-cumoquinol Me<sub>2</sub> ether could not be prepared. A. T. P.

Synthesis of substances related to the sterols. XL. (A) Preparation of 2:7-dihydroxyphenanthrene and derivatives. (B) Reduction of 1-γ-ketobutyl-2-naphthol. J. W. Cornforth and (Sir) R. Robinson (J.C.S., 1942, 684–689; cf. A., 1941, II, 365).—(A) Clemmensen reduction of 3:3'-dimethoxybenzoin (I), followed by hydrogenation of the crude product (contains 3:3'-dimethoxystilbene) in EtOH (Raney Ni) at normal temp. and pressure, gives 3:3'-dimethoxydibenzyl (II), also obtained from (I) and aq. C<sub>6</sub>H<sub>5</sub>N-CuSO<sub>4</sub> at 90–100°, followed by reduction and hydrogenation of the dimethoxybenzil. (II) is best prepared from *m*-OMe-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>Cl (improved prep.), by reaction of its Grignard reagent with anhyd. FeCl<sub>3</sub>. 3:3'-Dihydroxydibenzyl, m.p. 139–140°, is oxidised by FeCl<sub>3</sub> to yellow resins. (II) and Hg(OAc)<sub>2</sub>-AcOH-I at 50° afford 6:6'-di-iodo-3:3'-dimethoxydibenzyl, m.p. 113–114°, cyclised by Cu-bronze at ~260° to 2:7-dimethoxy-9:10-dihydrophenanthrene, m.p. 108–109°, which is dehydrogenated by S at 220–230° to 2:7-dimethoxyphenanthrene (III), m.p. 169–170°, converted by boiling HI-AcOH into the (OH)<sub>2</sub>-compound (IV) (dibenzoate, m.p. 252–253°) (not transformed into its Me ethers by HCl-MeOH). (IV) and Me<sub>2</sub>SO<sub>4</sub>-10% aq. NaOH-COMe<sub>2</sub> yield (III) and 2-hydroxy-7-methoxyphenanthrene (V), m.p. 173–174°, less readily prepared from the monobenzoate of (III) by methylation and hydrolysis. Hydrogenation (Cu chromite in EtOH) of (V) at 170–175°/100 atm. gives 2-hydroxy-7-methoxy-1:2:3:4-tetrahydrophenanthrene, m.p. 123–124°, with (probably) some 1:2:3:4:5:6:7:8-H<sub>8</sub>-derivative. 2:7-Dihydroxy-9:10-dihydrophenanthrene (VI), m.p. 206–208° (from the Me<sub>2</sub> ether and HI-AcOH), with BzCl at 210–220° gives the dibenzoate, m.p. 208–210°, and some monobenzoate; methylation of the latter with aq. COMe<sub>2</sub>-Me<sub>2</sub>SO<sub>4</sub>-NaOH, followed by alkaline hydrolysis, gives 2-hydroxy-7-methoxy-9:10-dihydrophenanthrene (VII), m.p. 118–120°. The Na derivative of (VII) and CO<sub>2</sub> at 210–220°/20 atm. yield 2-hydroxy-7-methoxy-9:10-dihydrophenanthrene-3-carboxylic acid, m.p. 225–226° (decomp.); 2:7-dihydroxy-9:10-dihydrophenanthrene-3:8-dicarboxylic acid, m.p. 305° (decomp.), is obtained from (VI) and CO<sub>2</sub> at 200°/5 atm. *m*-OMe-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-COCl (VIII), *p*-C<sub>6</sub>H<sub>4</sub>(OMe)<sub>2</sub>, and AlCl<sub>3</sub>-CS<sub>2</sub>, followed by Clemmensen reduction of the product and subsequent methylation, give 2:5:3'-trimethoxydibenzyl, b.p. 177–180°/0.4 mm. (demethylation gives tars). Me 2-hydroxy-4-phenylacetoxybenzoate, m.p. 53–54°, is obtained from 2:4:1-(OH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-CO<sub>2</sub>Me (IX) and CH<sub>2</sub>Ph-COCl-AlCl<sub>3</sub>-CS<sub>2</sub>, whereas condensation in PhNO<sub>2</sub> at 50–60° affords Me 2:4-dihydroxy-5-phenylacetylbenzoate, m.p. 150–151°, reduced (Clemmensen) to Me 2:4-dihydroxy-5-β-phenylethylbenzoate, m.p. 114–115° (aq. NaOH-EtOH give 4-β-phenylethylresorcinol). (VIII), (IX), and AlCl<sub>3</sub>-PhNO<sub>2</sub> at 30° afford a product, m.p. 165° (softens at 150°), hydrolysed by aq. NaOH-EtOH to an acid, m.p. 237–240°, which loses CO<sub>2</sub> at 240° to give 4-*m*-methoxyphenylacetylresorcinol, m.p. 109–110°. AlCl<sub>3</sub> or ZnCl<sub>2</sub>, (VIII), and methylumbelliferone at 140°, and then 170°, give no new product.

(B) Hydrogenation (Cu chromite-EtOH) of 1-γ-ketobutyl-2-naphthol (X) at 155°/75 atm. yields 2-hydroxy-1-γ-hydroxybutyl-1:2:3:4-tetrahydronaphthalene (XI), forms, m.p. 111–112°, and b.p. 215–220°/10 mm., but the corresponding diketone could not be obtained. XI is oxidised by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub>-aq. AcOH-C<sub>6</sub>H<sub>5</sub> to (probably) 1-hydroxy-2-keto-1-γ-ketobutyl-1:2:3:4-tetrahydronaphthalene, m.p. 79–80°. (XI) and Al(OBu<sup>n</sup>)<sub>3</sub>-C<sub>6</sub>H<sub>5</sub>-COMe, give a substance, b.p. 156–158°/9 mm., probably (A). (XI) and Al(OBu<sup>n</sup>)<sub>3</sub>-COMeEt-C<sub>6</sub>H<sub>5</sub> give a compound, b.p. 175–200°/15 mm., which affords a 2:4-dinitrophenylhydrazone, m.p. 212–213° (decomp.), probably derived from the diketone. (XI) and Raney Ni (N<sub>2</sub>) at 150–160° give *a*-methyltetrahydro-5:6-benzochroman, new m.p. 72–73°, also obtained from (X) by benzylation, followed by CH(OEt)<sub>2</sub>-HCl-EtOH, and hydrogenation (Raney Ni) of the 2-benzyloxy-1-γ-ketobutyl-naphthalene Et, acetal at 100°/100 atm. (X) and H<sub>2</sub>-Raney Ni-EtOH at 180°/125 atm. afford *perhydro*-2-methyl-5:6-benzochroman, b.p. 132–133°/9 mm., partly converted by an equal wt. of Ac<sub>2</sub>O



(+1% ZnCl<sub>2</sub>) at 200° into an unsaturated monoacetate, b.p. 167—172°/9 mm.  
A. T. P.

**Halogenation of phenolic ethers and anilides. XIII. Arrhenius activation energies for di- and poly-substituted aromatic ethers.**—See A., 1943, I, 38.

**Formation and rearrangement of *o*-tolyl benzhydryl ether.** H. A. Iddles, D. H. Chadwick, J. W. Clapp, and R. T. Hart (*J. Amer. Chem. Soc.*, 1942, **64**, 2154—2157).—Contrary to Schorigin (A., 1929, 183), the compound, m.p. 139—141°, obtained from *o*-cresol and CHPh<sub>2</sub>·OH in AcOH—H<sub>2</sub>SO<sub>4</sub> at 100°, is 3:5-dibenzhydryl-*o*-tolyl acetate (I); at room temp. 5-benzhydryl-*o*-cresol (II), m.p. 101°, b.p. 180—185°/2 mm., is obtained. *o*-C<sub>6</sub>H<sub>4</sub>Me·O·CHPh<sub>2</sub> (prep. from CHPh<sub>2</sub>Cl and *o*-C<sub>6</sub>H<sub>4</sub>Me·ONa in boiling Et<sub>2</sub>O), b.p. 175—178°/4 mm., with ZnCl<sub>2</sub> at 150° also gives (II). Br in CCl<sub>4</sub> converts (II) into the 3-*Br*-compound, m.p. 117—118°, which is also obtained (70%) from 1:3:2-C<sub>6</sub>H<sub>3</sub>MeBr·OH and CHPh<sub>2</sub>·OH in AcOH—H<sub>2</sub>SO<sub>4</sub> at room temp. With Me<sub>2</sub>SO<sub>4</sub>—NaOH at 40°, (II) gives the *Me* ether (67%), m.p. 74—76°, also obtained (43%) from 2:1:5-OMe·C<sub>6</sub>H<sub>3</sub>Me·MgBr by CHPh<sub>2</sub>Cl or (75%) from 2:1:5-OMe·C<sub>6</sub>H<sub>3</sub>Me·CPh<sub>2</sub>·OH by Zn dust in AcOH. 2:1:3-OH·C<sub>6</sub>H<sub>3</sub>Me·CPh<sub>2</sub>·OH and Zn—AcOH give 3-benzhydryl-*o*-cresol (70%), m.p. 76—78°, which with Br—CCl<sub>4</sub> gives the 5-*Br*-derivative (45%), m.p. 97—100° (acetate, m.p. 157—158°), also obtained (m.p. 100—103°) from 1:5:3-C<sub>6</sub>H<sub>3</sub>MeBr·OH and CHPh<sub>2</sub>·OH in AcOH—H<sub>2</sub>SO<sub>4</sub> at 100°. 2:1:3:5-OH·C<sub>6</sub>H<sub>3</sub>Me(CO<sub>2</sub>Me)<sub>2</sub> (modified prep.) and MgPhBr in boiling Et<sub>2</sub>O give an orange substance (75%), 5:1:3:2-CPh<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me(CPh<sub>2</sub>·OH)<sub>2</sub>O, m.p. 206—208°, reduced by Zn dust in boiling AcOH to 3:5-dibenzhydryl-*o*-cresol, amorphous, m.p. 50—60° [3:5-dinitrobenzoate, m.p. 206—207°; acetate = (I)].  
R. S. C.

**Quaternary salts from β'-dimethylamino-β-thymoxydiethyl ether.** C. W. Ferry, A. E. Ardis, and J. S. Buck (*J. Amer. Chem. Soc.*, 1942, **64**, 2232).—Na thymoxide or 6-chlorothymoxide with boiling (Cl[CH<sub>2</sub>]<sub>2</sub>)<sub>2</sub>O and then 33% NHMe<sub>2</sub>—MeOH at 145°/150 lb. give oily bases, which with RHal yield benzyl-, m.p. 122—123°, and *p*-chlorobenzyl-, m.p. 166—166.5°, -β-β'-thymoxyethoxyethyltrimethylammonium chloride, β-β'-6-chlorothymoxyethoxyethyltrimethylammonium iodide, m.p. 152°, *p*-chloro-, m.p. 160°, and *p*-bromo-, m.p. 156.5—157°, -benzyl-β-β'-6-chlorothymoxyethoxyethyltrimethylammonium chloride.  
R. S. C.

**Quaternary salts containing aryloxy-ethyl and -propyl groups.** W. S. Ide, R. Baltzly, and J. S. Buck (*J. Amer. Chem. Soc.*, 1942, **64**, 2234).—Na thymoxide and 6-chlorothymoxide with OH[CH<sub>2</sub>]<sub>n</sub>·Br give OH[CH<sub>2</sub>]<sub>n</sub>·X and thence (PBr<sub>3</sub>) Br[CH<sub>2</sub>]<sub>n</sub>·X and (NHMe<sub>2</sub>—MeOH; 120—125°) NMe<sub>2</sub>[CH<sub>2</sub>]<sub>n</sub>·X, which with AlkHal yield β-thymoxy-, m.p. 176°, and β-6-chlorothymoxy-ethyltrimethylammonium iodide, m.p. 228°, benzyl-, m.p. 194°, *p*-, m.p. 216°, and *o*-chlorobenzyl-, m.p. 175°, -β-6-chlorothymoxyethyltrimethylammonium chloride, γ-6-chlorothymoxy-*n*-propyltrimethylammonium iodide, m.p. 229°, *p*-chlorobenzyl-, m.p. 204°, and *p*-bromobenzyl-, m.p. 191°, -γ-6-chlorothymoxy-*n*-propyltrimethylammonium chloride, and di-γ-6-chlorothymoxy-*n*-propyltrimethylammonium chloride, m.p. 184—187°. β-6-Chlorothymoxyethyl-pyridinium, m.p. 119—120°, and -2:4-dimethylthiazolinium bromide, m.p. 214°, are prepared.  
R. S. C.

**Unsymmetrical disubstituted carbamides.** J. S. Buck, W. S. Ide, and R. Baltzly (*J. Amer. Chem. Soc.*, 1942, **64**, 2233).—NHRR' and NH<sub>2</sub>·CO·NH·NO<sub>2</sub> give *N*-methyl-*N*-*n*-hexyl-, m.p. 75°, *N*-*p*-anisyl-*N*-sec-butyl-, m.p. 140°, -β-methyl-*n*-butyl-, m.p. 130°, -ββ-dimethyl-*n*-propyl-, m.p. 155°, and -αγ-dimethyl-*n*-butyl-, m.p. 110°, -carbamide.  
R. S. C.

**5-Amino-2-hydroxybenzenesulphonamide and related compounds.** R. T. Williams (*J.C.S.*, 1942, 708—709).—5:2:1-NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(OH)·SO<sub>3</sub>H and C<sub>5</sub>H<sub>5</sub>N—Ac<sub>2</sub>O at room temp. afford C<sub>5</sub>H<sub>5</sub>N 5-acetamido-2-acetoxybenzenesulphonate, m.p. 143—144°, converted by PCl<sub>5</sub> into 5-acetamido-2-acetoxybenzenesulphonyl chloride (I), m.p. 148—149°. (I) and 50% aq. NH<sub>3</sub>, followed by cold 2N-HCl, yield 5-acetamido-2-hydroxybenzenesulphonamide, m.p. 215°, hydrolysed by boiling aq. HCl to the 5-NH<sub>2</sub>-compound, m.p. 202° (decomp.). 5-Acetamido-2-acetoxybenzenesulphonanilide, m.p. 150° (decomp.), obtained from (I) and NH<sub>2</sub>Ph—AcOEt, is hydrolysed by boiling 2N-HCl to 5-amino-2-hydroxybenzenesulphonanilide, m.p. 159°. 3:4:1-NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(OH)·SO<sub>3</sub>H gives C<sub>6</sub>H<sub>5</sub>N 3-acetamido-4-acetoxybenzenesulphonate, m.p. 162°, and thence the corresponding sulphonyl chloride (II), m.p. 143°, and 3-acetamido-4-acetoxy-, m.p. 205°, and 3-amino-4-hydroxy-benzenesulphonanilide, m.p. 172° (poor yield). (II) and aq. NH<sub>3</sub>, followed by hydrolysis with 2N-HCl, give a non-cryst. product. 4:2:1-NHAc·C<sub>6</sub>H<sub>3</sub>(OAc)·SO<sub>2</sub>Cl gives 4-acetamido-2-acetoxy-, m.p. 213—214°, whence 4-amino-2-hydroxy-benzenesulphonanilide, m.p. 184°.  
A. T. P.

**Vital stains. I.** A. A. Goldberg (*J.C.S.*, 1942, 713—716).—Vital stains of the trypan-blue type, containing I or As, are synthesised. 5:1:2-C<sub>6</sub>H<sub>3</sub>Ime·N<sub>2</sub>Cl and 8:3:6:1-OH·C<sub>10</sub>H<sub>4</sub>(SO<sub>3</sub>Na)<sub>2</sub>·NH<sub>2</sub> (I) in aq. NaOH at 0—5°, then at 40°, give Na<sub>2</sub> 1-amino-2-(5'-iodo-*o*-tolueneazo)-8-naphthol-3:6-disulphonate, which with tetrazotised *o*-tolidine in NaOH affords Na<sub>4</sub> 3:3'-dimethyldiphenyl-4:4'-bis-

[2''-azo-8''-amino-1''-hydroxy-3'' : 6''-disulphonaphthalene-7''-(5'''-iodo-*o*-azotoluene)]; the benzidine and dianisidine analogues are prepared. 1:2:6:4-N<sub>2</sub>Cl·C<sub>6</sub>H<sub>4</sub>I<sub>2</sub>·AsO<sub>3</sub>H<sub>2</sub> and (I) afford Na<sub>2</sub> 1-amino-2-(2' : 6'-di-iodo-4'-arsonobenzeneazo)-8-naphthol-3:6-disulphonate, converted into Na<sub>2</sub> 3:3'-dimethyldiphenyl-4:4'-bis-[2''-azo-8''-amino-1''-hydroxy-3'' : 6''-disulphonaphthalene-7''-(azo-2''' : 6'''-di-iodobenzene-4'''-arsonate)]. CH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>·*p*)<sub>2</sub> and 1-CaCO<sub>3</sub>·H<sub>2</sub>O—Et<sub>2</sub>O give 3:3'-di-iodo-4:4'-diaminodiphenylmethane, m.p. 80—85°, which is tetrazotised and coupled with K<sub>2</sub> 2-amino-1-(4'-arsonobenzeneazo)-8-naphthol-3:6-disulphonate to give K<sub>2</sub> 3:3'-di-iododiphenylmethane-4:4'-bis-(2''-azo-7''-amino-1''-hydroxy-3'' : 6''-disulphonaphthalene-8''-azobenzene-4'''-arsonate). 4:2:6:1-SO<sub>3</sub>H·C<sub>6</sub>H<sub>4</sub>I<sub>2</sub>·N<sub>2</sub>Cl and (I) afford Na<sub>2</sub> 1-amino-2-(2' : 6'-di-iodo-4'-sulphobenzeneazo)-8-naphthol-3:6-disulphonate (II). Benzidine-2:2'-disulphonic acid in aq. NaOH at 80°, added to ICl—aq. HCl at 80°, affords Na<sub>2</sub> 5:5'-di-iodobenzidine-2:2'-disulphonate (III), which (tetrazotised) with (II) gives Na<sub>2</sub> 5:5'-di-iodo-2:2'-disulphodiphenyl-4:4'-bis-[2''-azo-8''-amino-1''-hydroxy-3'' : 6''-disulphonaphthalene-7''-(azo-2''' : 6'''-di-iodobenzene-4'''-sulphonate)]. 1:4:6:2-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>I<sub>2</sub>·CO<sub>2</sub>H, m.p. 228—230° (from *o*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Na and ICl—aq. HCl, at 70—80°), gives Na<sub>2</sub> 1-amino-2-(2' : 4'-di-iodo-6'-carboxybenzeneazo)-8-naphthol-3:6-disulphonate, and thence, with tetrazotised (III), Na<sub>2</sub> 5:5'-di-iodo-2:2'-disulphodiphenyl-4:4'-bis-[2''-azo-8''-amino-1''-hydroxy-3'' : 6''-disulphonaphthalene-7''-(azo-2''' : 4'''-di-iodobenzene-6'''-carboxylate)].  
A. T. P.

**Condensation of *o*-, *m*-, and *p*-thiocresols with *o*-bromonitrobenzene, 2:5-dichloro- and 2:5-dibromo-nitrobenzene.** P. S. Varma, K. S. V. Raman, and N. H. Malani (*J. Indian Chem. Soc.*, 1942, **19**, 354—356).—C<sub>6</sub>H<sub>4</sub>Me·SNa (or K) and the halogen compounds (with Cu-bronze for *o*-C<sub>6</sub>H<sub>4</sub>Br·NO<sub>2</sub>) at ~180—200° give 2'-nitro-2-, b.p. 210—215°/16 mm., m.p. 86°, -3-, b.p. 222°/18 mm., m.p. 86.5°, and -4-methyl-, m.p. 87.5°, 4-chloro-, m.p. 121°, and 4-bromo-2-nitro-4'-methyl-, m.p. 124°, and 4-chloro-2-nitro-2'-methyl-diphenyl sulphide, b.p. 200—205°/18 mm., m.p. 82.5°. 4-Bromo-2-nitro-4'-methyldiphenyl sulphone has m.p. 132°.  
F. R. S.

**Energy-level treatment of reaction data.**—See A., 1943, I, 38.

**Acid-catalysed hydrolysis of phenyl-substituted aliphatic esters.**—See A., 1943, I, 39.

**Isethionic acid.** A. A. Goldberg (*J.C.S.*, 1942, 716—718).—Isethionic acid is obtained from Et<sub>2</sub>SO<sub>4</sub> and 60% oleum at >10°, with subsequent hydrolysis (H<sub>2</sub>O) and is isolated as the Ca salt. Na *O*-phenylacetyl-, *O*-β-phenylpropionyl-, and *O*-acetylmandelyl-isethionate [from Na isethionate and the acid chloride at 140° (alone in the first case) or in xylene] are hydrolysed slowly in neutral, more rapidly in acid, and very rapidly in strongly alkaline solution. Pharmacological applications of these are discussed, and lethal dosages for mice are given.  
A. Li.

**Manufacture of hydroxylamine and mandelic acid.**—See B., 1943, II, 5.

**Preparation of substituted mandelic acids and their bacteriological effects. III.** J. L. Riebsomer, D. Stauffer, F. Glick, and F. Lambert (*J. Amer. Chem. Soc.*, 1942, **64**, 2080—2081; cf. A., 1939, II, 62).—Figures in parentheses below are bacteriological activities relative to OH·CHPh·CO<sub>2</sub>H. CO(CO<sub>2</sub>Et)<sub>2</sub>, the appropriate hydrocarbon, and SnCl<sub>4</sub> give OH·CAr(CO<sub>2</sub>Et)<sub>2</sub>, in which Ar = 2:4:1-, b.p. 150—155°/4—5 mm., 3:4:1-, b.p. 157—160°/4—5 mm., and 2:5:1-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>, b.p. 154—156°/4—5 mm., *p*-CH<sub>2</sub>Ph·C<sub>6</sub>H<sub>4</sub>, b.p. 225—230°/4—5 mm., and *p*-C<sub>6</sub>H<sub>4</sub>Ph, converted by 20% KOH and then aq. HCl into -2:4- (3.5), m.p. 113—115° [acetate (0.5), m.p. 92°], 3:4- (3.5), m.p. 135°, and 2:5-dimethyl- (3.5), m.p. 116.5—117° [acetate (<1), m.p. 112—113°; propionate (<1), m.p. 86°], *p*-benzyl- (<1), m.p. 133.5—134.5°, and *p*-phenyl-mandelic acid (0), m.p. 192° [acetate (0), m.p. 133°; propionate (0), m.p. 107°]. Structures are proved by oxidation to the expected benzoic acid. 2-C<sub>10</sub>H<sub>7</sub>Me gives a very poor yield of an acid, m.p. 146.5—147.5°. CHPh<sub>3</sub> gives an impure acid, m.p. 90—95°; 1-C<sub>10</sub>H<sub>7</sub>Me, fluorene, acenaphthene, and anthracene do not give the expected acids. Crude xylene gives a product as active as the isomerides but too toxic. Mandelic acid acetate (1), m.p. 76—76.5°, and propionate (2), m.p. 58°, and *p*-methylmandelic acid acetate (0.5), m.p. 104—105°, are also reported.  
R. S. C.

**Condensations of γ-bromocrotonic esters with zinc.** K. Ziegler, W. Schumann, and E. Winkelmann (*Annalen*, 1942, **551**, 120—126; cf. Fuson *et al.*, A., 1938, II, 442).—CH<sub>2</sub>Br·CH·CH·CO<sub>2</sub>Me, PhCHO, and Zn wool in boiling C<sub>6</sub>H<sub>6</sub> readily give *Me* δ-hydroxy-δ-phenyl-Δ<sup>α</sup>-pentenoate, b.p. 175—179°/11 mm., which absorbs 1 H<sub>2</sub> (Pd—BaSO<sub>4</sub> in EtOAc) giving a product dehydrated (KHSO<sub>4</sub> at 150—170°) to CHPh·CH[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>Me, b.p. 158—162°/10 mm., m.p. 75°, which is hydrogenated and then hydrolysed to Ph[CH<sub>2</sub>]<sub>4</sub>·CO<sub>2</sub>H. CHPh·CH·CHO similarly gives a little Ph[CH·CH]<sub>3</sub>·CO<sub>2</sub>Me. CH<sub>2</sub>Br·CMe·CH·CO<sub>2</sub>Me (I) and PhCHO readily afford essentially *Me* δ-hydroxy-δ-phenyl-β-methyl-Δ<sup>α</sup>-pentenoate, b.p. 192—203°/14 mm. (64%), hydrolysed to the acid, m.p. 154°, and hydrogenated (Pd—BaSO<sub>4</sub> in abs. EtOH) to OH·CHPh·CH<sub>2</sub>·CHMe·CH<sub>2</sub>·CO<sub>2</sub>Me, m.p. 65°; it is converted by PBr<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> at room temp. into *Me*

$\delta$ -bromo- $\delta$ -phenyl- $\beta$ -methyl- $\Delta^a$ -pentenoate, which with collidine under  $N_2$  at  $110^\circ$  gives the Me ester, b.p.  $173$ — $181^\circ/12$  mm., of  $\delta$ -phenyl- $\beta$ -methyl- $\Delta^{ar}$ -pentadienoic acid, m.p.  $157^\circ$ , hydrogenated to  $\delta$ -phenyl- $\beta$ -methyl- $n$ -valeric acid.  $\epsilon$ -Phenyl- $\beta$ -methyl- $\Delta^{ab\delta}$ -hexatrienoic acid, m.p.  $192^\circ$ , is obtained by hydrolysing the distilled product from (I) and  $CHPh\cdot CH\cdot CHO$ . H. W.

**Lactones related to the cardiac aglycones. X. Synthesis of simple, hydroxylated  $\beta$ -substituted  $\Delta^{ab}$ -butenolides.** E. R. Marshall, J. A. Kuck, and R. C. Elderfield (*J. Org. Chem.*, 1942, 7, 444—456).—Dropwise addition of  $CH_2Br\cdot CO_2Et$  in  $C_6H_6$  to a boiling mixture of  $p$ -OMe- $C_6H_4\cdot CO\cdot CH_2\cdot OMe$ ,  $C_6H_6$ , and Zn gives *Et*  $\beta$ -hydroxy- $\gamma$ -methoxy- $\beta$ - $p$ -anisylbutyrate (I), b.p.  $152$ — $160^\circ/0.6$  mm., which does not absorb  $H_2$  in EtOH containing  $PtO_2$ . The corresponding acid, m.p.  $102.5$ — $103.5^\circ$ , is transformed by  $HBr\cdot AcOH$  at  $110$ — $120^\circ$  into  $\beta$ - $p$ -anisyl- $\Delta^{ab}$ -butenolide [ $\beta$ - $p$ -anisyl- $\Delta^a$ -butenolactone] (II), m.p.  $120^\circ$ , demethylated by  $AcOH\cdot HBr$  at  $120$ — $140^\circ$  to (slightly impure)  $\beta$ - $p$ -hydroxyphenyl- $\Delta^{ab}$ -butenolide (III), m.p.  $262.5$ — $263.5^\circ$  (sealed capillary) (acetate, m.p.  $138.6$ — $140.7^\circ$ ), also obtained directly from (I).  $p$ -OAc- $C_6H_4\cdot COCl$  is transformed by successive treatments with  $CH_2N_2$  and  $AcOH$  into  $p$ -OAc- $C_6H_4\cdot CO\cdot CH_2\cdot OAc$ , m.p.  $94.6$ — $95.6^\circ$ , which is converted by Zn and  $CH_2Br\cdot CO_2Et$  followed by hydrolysis into (III), which gives a strong Legal test and with  $CH_2N_2$  gives (II).  $m$ -OAc- $C_6H_4\cdot CO_2H$  is transformed through the chloride,  $CHN_2$  ketone, and  $m$ -OAc- $C_6H_4\cdot CO\cdot CH_2\cdot OAc$  into  $\beta$ - $m$ -hydroxyphenyl- $\Delta^{ab}$ -butenolide, m.p.  $187.5$ — $188.5^\circ$  (sealed capillary), which gives a positive Legal test, a colour with  $FeCl_3$ , and decolorises  $Br\cdot H_2O$ ; the Me ether, m.p.  $86.3$ — $87.3^\circ$ , gives a positive Legal but negative  $FeCl_3$  test.  $o$ -OAc- $C_6H_4\cdot CO\cdot CHN_2$  is converted by glacial  $AcOH$  into coumaranone (IV), also formed with an orange compound, m.p.  $204$ — $205^\circ$ , using  $AcOH$  at room temp. and subsequently at  $100^\circ$ .  $o$ -OMe- $C_6H_4\cdot CO\cdot CHN_2$  reacts violently with  $AcOH$  in absence of a solvent but smoothly in presence of  $Et_2O$  to give (IV).  $o$ -OMe- $C_6H_4\cdot MgBr$  and  $OMe\cdot CH_2\cdot CN$  afford  $o$ -OMe- $C_6H_4\cdot CO\cdot CH_2\cdot OMe$ , b.p.  $149$ — $152^\circ/10$  mm. (semicarbazone, m.p.  $138.1$ — $139.1^\circ$ ), converted into *Et*  $\beta$ -hydroxy- $\gamma$ -methoxy- $\beta$ - $o$ -anisylbutyrate (V), b.p.  $127$ — $128^\circ/0.2$  mm., and thence into  $\beta$ - $o$ -anisyl- $\Delta^{ab}$ -butenolide, m.p.  $95.1$ — $95.6^\circ$ ; this is transformed by  $HBr$ ,  $HBr\cdot AcOH$ , or  $AcOH$  under varied conditions into coumaronyl-3-acetic acid, m.p.  $89.2$ — $91.2^\circ$ , mixed with unchanged material. Reduction ( $PtO_2$  in  $AcOH$ ) of (V) yields *Et*  $\beta$ -hydroxy- $\gamma$ -methoxy- $\beta$ -2-methoxycyclohexylbutyrate, b.p.  $122$ — $123^\circ/1$  mm., with some hexahydrocoumaronyl derivatives; the ester does not react satisfactorily with  $HCl$  or  $HBr$ .  $o$ -OMe- $C_6H_4\cdot CO_2Me$  is hydrogenated (Raney Ni) at  $200^\circ/2000$ — $2700$  lb. per sq. in. to Me 2-methoxycyclohexanecarboxylate, b.p.  $96.5$ — $97^\circ/15$  mm. (but mainly to Me cyclohexanecarboxylate), converted into the acid, b.p.  $122$ — $123^\circ/5$  mm. (*p*-toluidide, m.p.  $130.2$ — $132.4^\circ$ ), the acid chloride,  $\omega$ -diazo- $o$ -methoxyhexahydroacetophenone, and thence into a mixture of hexahydrocoumaranone and  $\omega$ -acetoxy- $o$ -methoxyhexahydroacetophenone. High-pressure hydrogenation of  $o$ -OH- $C_6H_4\cdot CO_2Me$  in EtOH gives *Et* hexahydroisocoumarate, b.p.  $110$ — $115^\circ/13$  mm., hydrolysed to a mixture of acids, m.p.  $76$ — $78^\circ$  and  $109$ — $110^\circ$ , and transformed by  $NH_3$  into the amide, m.p.  $113.7$ — $114.7^\circ$ . The crude acid is transformed by  $AcCl$  in boiling  $Et_2O$  followed by distillation into 2-acetoxycyclohexanecarboxylic acid, m.p.  $66.1$ — $66.6^\circ$  (*p*-toluidides, m.p.  $154$ — $155.9^\circ$  and  $124$ — $143^\circ$ ). The crude acid is transformed into the chloride and thence into the  $CHN_2$  ketone, which could not be satisfactorily converted into  $\omega$ : $o$ -diacetoxyhexahydroacetophenone. None of the lactones described above shows cardiac activity when tested in frogs. M.p. are corr. H. W.

**Preparation of hexahydro-*p*-toluamides.** M. Delépine and M. Badoche (*Ann. Chim.*, 1942, [xi], 17, 179—182).—*p*-Toluic acid is hydrogenated ( $PtO_2\cdot AcOH$ ) to the  $H_6$ -derivative (I), b.p.  $128$ — $130^\circ/13$  mm., partly converted by  $HCl$  at  $235$ — $240^\circ$  for 2 hr. into the *trans*-acid, m.p.  $111^\circ$  (60% yield) [amide, m.p.  $226^\circ$  (block)]. (I) is a mixture, consisting mainly of *cis*-hexahydro-*p*-toluic acid [amide, m.p.  $163^\circ$  (block) or  $160$ — $160.5^\circ$  (tube)]. Other m.p. (lit.) of the amides are those of mixtures. A. T. P.

**Basic indium salicylates.** T. Moeller (*J. Amer. Chem. Soc.*, 1942, 64, 2234).—Anhyd.  $In_2(SO_4)_3$  (1 mol.) and  $o$ -OH- $C_6H_4\cdot CO_2Na$  (3 mols.) in  $H_2O$  gives basic In salicylate,  $In(C_7H_5O_3)_2\cdot OH$ , +  $3H_2O$ , converted at  $110^\circ$  or in boiling MeOH into the anhyd. salt. R. S. C.

**Chloralamides. Chloral-5-acetamidosalicylamide and related compounds.** K. N. Rana (*J. Indian Chem. Soc.*, 1942, 19, 299—302).—5-Acetamidosalicylamide (+ $H_2O$ ), m.p.  $204$ — $206^\circ$  (loses  $H_2O$  at  $110^\circ$ ) [from 5:2:1-NHAc- $C_6H_3(OH)\cdot CO_2Me$  and aq.  $NH_3$ ], heated with chloral yields 5-acetamidosalicyl- $\beta\beta\beta$ -trichloro- $\alpha$ -hydroxyethylamide, m.p.  $176$ — $177^\circ$  (decomp.) [violet colour with  $FeCl_3$ ; Me<sub>2</sub> ether (Me<sub>2</sub>SO<sub>4</sub>), m.p.  $166$ — $167^\circ$ ; Bz<sub>2</sub> m.p.  $187$ — $188^\circ$ , and Ac<sub>2</sub> derivative (Ac<sub>2</sub>O), m.p.  $212$ — $214^\circ$ ], dehydrated (cold conc.  $H_2SO_4$ ) to 6-acetamido-2-trichloromethylbenzometoxazone, m.p.  $218$ — $219^\circ$  (Ac derivative, m.p.  $197$ — $198^\circ$ ). Formation and stability of 5-substituted chloralsalicylamides are promoted by positive substituents. A. Li.

**Diamino-peptides.** R. Baltzly, W. S. Ide, and J. S. Buck (*J. Amer. Chem. Soc.*, 1942, 64, 2231).—Hydrogenation of

$NMe_2\cdot [CH_2]_2\cdot CO\cdot NH\cdot C_6H_4\cdot NO_2\cdot p$  (prep. from  $Br\cdot [CH_2]_2\cdot CO\cdot NH\cdot C_6H_4\cdot NO_2\cdot p$  and  $NHMe_2$ ) (hydrochloride, m.p.  $200$ — $201^\circ$ ) and its methochloride in  $HCl\cdot EtOH$  gives  $\beta$ -dimethylaminopropion-*p*-aminoanilide dihydrochloride, m.p.  $218$ — $219^\circ$ , and the corresponding methochloride hydrochloride, m.p.  $211$ — $212^\circ$ , respectively.  $NEt_2\cdot [CH_2]_2\cdot NH_2$  (prep. from  $NEt_2\cdot CH_2\cdot CN$  by  $Na\cdot EtOH$ ) gives the *p*-NO<sub>2</sub>- $C_6H_4\cdot CO$  derivative hydrochloride, m.p.  $164$ — $165^\circ$ ; this and its ethochloride yield (hydrogenation) *N*-*p*-aminobenzoyl-*N'*-diethylethylenediamine dihydrochloride, m.p.  $176.5$ — $178^\circ$ , and the corresponding ethochloride hydrochloride, m.p.  $228^\circ$ , respectively.  $NMe_2\cdot [CH_2]_2\cdot CN$  gives similarly  $NMe_2\cdot [CH_2]_3\cdot NH_2$  (dihydrochloride, m.p.  $182$ — $184^\circ$ ; *p*-NO<sub>2</sub>- $C_6H_4\cdot CO$  derivative hydrochloride, m.p.  $190$ — $192^\circ$ ), and *N*-*p*-aminobenzoyl-*N'*-dimethyltrimethylenediamine dihydrochloride, m.p.  $184$ — $185^\circ$ . The *p*-nitrophenylcarbamate of  $OH\cdot [CH_2]_2\cdot NEt_3Cl$  is reduced to the *p*-aminophenylcarbamate (hydrochloride, m.p.  $138$ — $139^\circ$ ). R. S. C.

**Action of thionyl chloride on 2:3-hydroxynaphthoic acid.** J. W. Airan and S. V. Shah (*J. Indian Chem. Soc.*, 1942, 19, 333—334).—2:3-OH- $C_{10}H_7\cdot CO_2H$  (I) with  $SOCl_2$  at  $110^\circ$  yields the lactone, m.p.  $240^\circ$ , hydrolysed (dil.  $NaOH$ ) to (I). A. Li.

**Reaction of furoic acid with aromatic compounds. II. Reaction of methyl furoate with benzene and chlorobenzene.** C. C. Price and C. F. Huber. III. C. C. Price, E. C. Chapin, and M. Rieger (*J. Amer. Chem. Soc.*, 1942, 64, 2136—2139, 2227—2228; cf. A., 1941, II, 291).—II. Me furoate,  $C_6H_6$ , and  $AlCl_3$  at  $0^\circ$  and later  $70^\circ$  give 1- $C_{10}H_7\cdot CO_2Me$  (32—46%) (cf. McCorkle *et al.*, *Proc. Iowa Acad. Sci.*, 1936, 43, 205) and a tar, containing Me 9-ethyl-9:10-dihydro-9-anthroate (I) (11—20%), m.p.  $52$ — $54^\circ$ , b.p.  $144$ — $145^\circ/0.04$  mm., but with  $PhCl$  at  $0^\circ$  and later  $90$ — $100^\circ$  gives 6:1- $C_{10}H_6Cl\cdot CO_2H$  (~40%) and its Me ester (15%). Formation of (I) involves reductive fission of the *endo*- $[CH_2]_2$  bridge. The structure of (I) is proved by conversion into anthracene (II) (61%) by soda-lime at slightly  $>360^\circ$  and by oxidation by  $CrO_3\cdot AcOH\cdot H_2O$  to anthraquinone (III) (80%) or by less  $CrO_3$  to Me 9-ethyl-10-anthrone-9-carboxylate (35%) (2:4-dinitrophenylhydrazones, m.p.  $215^\circ$ ; isolated by Girard's reagent T), and by resistance to hydrolysis.

III. The crude acids obtained from furoic acid (IV) and  $C_6H_6$  by  $AlCl_3$  (*loc. cit.*) probably contain 9-ethyl-9:10-dihydro-9-anthroic acid, since by oxidation they give (III) and by distillation with soda-lime give (II) (10%) with an oil, which with S gives 1:4- $C_{10}H_6Ph_2$ . The acids from (IV) and  $PhMe$  give, by soda-lime, 2:7-dimethylantracene (from 3:6-dimethyl-9-ethyl-9:10-dihydro-9-anthroic acid), but only tars by other methods. R. S. C.

**Synthesis of phthalides from 3:4:5-trimethoxybenzoic acid.** F. E. King and T. J. King (*J.C.S.*, 1942, 726—727).—3:4:5:1-(OMe)<sub>3</sub>- $C_6H_2\cdot CO_2H$ , aq. 40%  $CH_2O$ , and conc.  $HCl$  at  $140^\circ$  yield 3:4:5-trimethoxyphthalide (I) or (more  $HCl$ ) its 6- $CH_2Cl$  derivative (II), m.p.  $85^\circ$  [also obtained from (I),  $CH_2O$ , and conc.  $HCl$ ]; in each case ~5% of 6:6'-methylenebis-3:4:5-trimethoxyphthalide (III), m.p.  $199^\circ$ , is isolable. (I) with  $NaOEt$  and  $Et_2C_2O_4$  in  $PhMe$  and  $N_2$  at  $100^\circ$  (bath) affords *Et* 3:4:5-trimethoxyphthalidylglyoxylate, m.p.  $188$ — $189^\circ$ . With  $CH_2O$  and  $HCl$ , syringic acid yields 4-hydroxy-3:5-dimethoxy-6-chloromethylphthalide, m.p.  $185^\circ$ , and 6:6'-methylenebis-4-hydroxy-3:5-dimethoxyphthalide, m.p.  $223$ — $224^\circ$  [methylated to (III)], whilst 2:3:4:1-OH- $C_6H_2(OMe)_2\cdot CO_2H$  gives only 5:5'-methylenebis-2-hydroxy-3:4-dimethoxybenzoic acid, m.p.  $252^\circ$  (efferv.). A. Li.

**Kinetics and equilibria of the carbinol formation of phenolphthalein.**—See A., 1943, I, 39.

**Monoperphthalic acid.**—See B., 1943, II, 5.

**Synthesis of 3-hydroxyphthalic acid.** O. Gisvold (*J. Amer. Pharm. Assoc.*, 1942, 31, 202—203).—3:1:2-NO<sub>2</sub>- $C_6H_3(CO_2H)_2$  is hydrogenated (Pt-black or Raney Ni in EtOH) to the  $NH_2$ -acid, converted (diazo-method) into 3:1:2-OH- $C_6H_3(CO_2H)_2$ , m.p.  $154^\circ$  (lit.  $151^\circ$ ,  $244^\circ$ ) [anhydride, m.p.  $195^\circ$  (lit.  $198$ — $199^\circ$ )]. J. E. P.

**Inhibition of oxidation of aldehydes.**—See A., 1943, III, 36.

**Kinetics of oxidation of aldehydes by chromic acid. III. Oxidation of tolualdehydes. IV. Oxidation of bromobenzaldehydes.**—See A., 1943, I, 38.

**Behaviour of pyrogallol trimethyl ether and 3:4:5-trimethoxybenzonitrile with Grignard reagents.** C. D. Hurd and H. E. Winberg (*J. Amer. Chem. Soc.*, 1942, 64, 2085—2086).—3:4:5:1-(OMe)<sub>3</sub>- $C_6H_2\cdot CN$  (prep. outlined) and  $MgBu^tBr$  in boiling  $PhMe$  give mainly 4:3:5:1-OH- $C_6H_2(OMe)_2\cdot COBu^t$  (I) (cf. Haller *et al.*, A., 1939, II, 508), but in  $Et_2O\cdot PhMe$  at  $40^\circ$  give only 3:4:5:1-(OMe)<sub>3</sub>- $C_6H_2\cdot COBu^t$  (II), b.p.  $164$ — $166^\circ/6$  mm., m.p.  $37$ — $39^\circ$ . The structure of (I) is shown by prep. from (II) by  $H_2SO_4$  at  $35$ — $40^\circ$  and by oxidation ( $CrO_3\cdot AcOH$ ) to 1:2:6:4-O- $C_6H_2(OMe)_2\cdot O$ . 1:2:3- $C_6H_3(OMe)_3$  and  $MgMeI$  in boiling  $PhMe$  give 2:6:1-(OMe)<sub>3</sub>- $C_6H_3\cdot OH$ . R. S. C.

**Synthesis of 2-substituted phenanthrenes.** B. Riegel, M. H. Gold, and M. A. Kubico (*J. Amer. Chem. Soc.*, 1942, 64, 2221—2222).—2-Substituted phenanthrenes are best (2-Ac 53, -EtCO 45, -Pr<sup>CO</sup> 48, -CO<sub>2</sub>Me- $[CH_2]_2\cdot CO$  70, and -NH<sub>2</sub> 25%) prepared by dehydro-

generating the corresponding readily available 9:10- $H_2$ -derivatives by S at, e.g., 250—280°. 2-isoButyryl-9:10-dihydrophenanthrene, m.p. 71.6—72.6°, and -phenanthrene, m.p. 116.8—117.6°, and Me  $\gamma$ -keto- $\gamma$ -2-phenanthryl-n-butyrate, m.p. 112.2—112.6°, are described. M.p. are corr. R. S. C.

**Photochemical reactions of ketones. II. Benzpinacol and benzpinacolin.** A. Banchetti (*Gazzetta*, 1941, 71, 685—693).—The reduction of  $COPh_2$  in  $Pr^iOH-HCl$  in sunlight gives  $(CPh_2 \cdot OH)_2$  (I), tetraphenylethylene oxide (II), and  $CPh_3Bz$  (III), in proportions depending on acidity and temp. In  $Et_2O-HCl$  in sunlight, (II) is formed. Mechanisms are discussed. With  $P_2O_5$  in boiling  $C_6H_6$ , (I) gives (III). In boiling  $EtOH$  containing some dil.  $HCl$ , (I) is unchanged. E. W. W.

**Synthesis of o-o'-anisoylbenzoic acid.** B. P. Geyer (*J. Amer. Chem. Soc.*, 1942, 64, 2226—2227).—Adding o- $OMe \cdot C_6H_4 \cdot MgBr$  (prep. from Mg activated by  $EtBr$ ) in  $Et_2O$  to o- $C_6H_4(CO)_2O$  in  $C_6H_6$  gives o- $CO_2H \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot OMe-o$  (54%), m.p. 143—143.5°, and  $\alpha\alpha$ -di-o-anisylphthalide (18%), m.p. 148—149°. R. S. C.

**Amino-alcohols. XI. Arylglyoxylohydroxamyl chlorides.** N. Levin and W. H. Hartung (*J. Org. Chem.*, 1942, 7, 408—415).— $COAr \cdot CCl_2N \cdot OH$  (I) are obtained by gradual addition of alkyl nitrite to a solution of  $COAr \cdot CH_2Cl$  in  $Et_2O$  through which  $HCl$  is slowly passing. (I) are converted into  $OH \cdot N \cdot CAR \cdot CCl_2N \cdot OH$  by  $NH_2OH \cdot HCl$  in aq.  $EtOH$  at room temp. Thus are obtained phenylglyoxylohydroxamyl chloride (II), m.p. 132—133°, and the corresponding chloroglyoxime, decomp. 186—187°. The following derivation of (II) have been obtained; the m.p. of the corresponding chloroglyoximes are placed in parentheses: p-methyl-, m.p. 126—128° (decomp. 185—186°); p-phenyl-, m.p. 157—158° (decomp. 177°); p-chloro-, m.p. 120—121° (decomp. 181—182°); p-methoxy-, m.p. 137—139°; p-hydroxy-, decomp. 158—159° (decomp. 183—184°); 3:4-dihydroxy-, decomp. 184—185°. Alkaline decomp. of (I) gives the corresponding benzoic acids in excellent yield. (I) and  $NH_2Ph$  in anhyd.  $Et_2O$  at room temp. give the corresponding anilides; phenylglyoxylohydroxamylamide, m.p. 145—146° (decomp.), and its p-methyl-, m.p. 163—164° (decomp.), p-phenyl-, m.p. 135—136° (decomp.), p-chloro-, m.p. 145—146° (decomp.), p-methoxy-, m.p. 148—150° (decomp.), p-hydroxy-, m.p. 164—165° (decomp.), and 3:4-dihydroxy-, m.p. 155°, -derivatives are described. (I) appear to be catalytically hydrogenated to phenylethanamine and its derivatives. H. W.

**Dioximes. CXXV.** G. Ponzio (*Gazzetta*, 1941, 71, 693—695).—The compound, m.p. 108°, regarded by Avogadro (A., 1924, i, 294) as oximino-p-tolylacetone nitrile oxide (I), is  $\alpha$ -p-tolylglyoxime peroxide [3-p-tolyl-1:2:5-oxadiazole 5-oxide] (II); this in  $Et_2O$  with aq.  $Na_2CO_3$  gives (I), m.p. 112°, which, unlike (II), with conc.  $HCl$  readily gives p-tolylchloroglyoxime, p- $C_6H_4Me \cdot C(N \cdot OH) \cdot CCl_2N \cdot OH$ . With  $HCl-Et_2O$ , benzoyloximino-p-tolylacetone nitrile oxide gives p- $C_6H_4Me \cdot C(N \cdot OBz) \cdot CCl_2N \cdot OH$ . E. W. W.

**Enediols. X. An aminostilbenediol.** R. C. Fuson and S. L. Scott (*J. Amer. Chem. Soc.*, 1942, 64, 2152—2153; cf. A., 1942, II, 91).—(2:6:1- $C_6H_3Me_2 \cdot CO$ )<sub>2</sub> and  $HNO_3$  (d 1.59) at 0° give the 3:3'-( $NO_2$ )<sub>2</sub>- (I) (92%), m.p. 211—212° (corr.), and 3:5:3':5'-( $NO_2$ )<sub>4</sub>-derivative (1%), m.p. 273—275° (decomp.), and a substance, m.p. 241—243° (decomp.; corr.). (I) does not form an oxime or react with  $NHPh \cdot NH_2$ .  $H_2-PtO_2$  reduces (I) in  $EtOH$  slowly to colourless [3:2:6:1- $NH_2 \cdot C_6H_3Me_2 \cdot C(OH)_2$ ] (II), which is oxidised with great ease to 3:3'-diamino-vic.-xylil, m.p. 201—202° (corr.) ( $Ac_2$  derivative, m.p. 296—297°). (II) yields a hydrochloride (III), which with aq.  $NaOH$  gives an orange substance, m.p. 229—230° (decomp.; corr.). (III) with  $Ac_2O-C_5H_5N$ , or (II) with boiling  $Ac_2O$ , gives  $\alpha\beta$ -diacetoxy- $\alpha\beta$ -di-3-diacetamido-vic.-xylylethylene, m.p. 241—242° (corr.). 3- $NH_2$  thus does not affect the stability of the enediol. R. S. C.

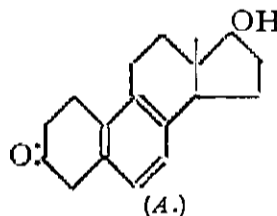
**Absorption spectra and structures of pyrethrins I and II.**—See A., 1943, I, 31.

**Structures of highly arylated indenones. Their behaviour with bromine.** C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1942, 64, 2127—2130).—2:3:5:6-Tetraphenylindanone (I) and Br in  $CHCl_3$  give (probably) 2-bromo- (II) (84%), m.p. 241° (decomp.), and then 2:7a-dibromo-2:3:5:6-tetraphenyl-2:7a-dihydroindenone (III), m.p. 270° (decomp.), which is also obtained (75%) from (I) by 2 mols. of Br.  $KI-AcOH$ ,  $KOH-EtOH$ , or  $MgRX$  reduces (III) to (II), but  $Zn-AcOH$  yields (I).  $HBr$  has no effect on (II) or (III); (II) may be formed by allylic rearrangement.  $(CH \cdot CO)_2O$  does not add to (II) or (III). With  $MgPhBr$  and then aq.  $NH_4Cl$ , (II) gives 2:3:5:6-tetraphenyl-2:7a-dihydroindenone (50%), m.p. 125° (instantaneous) or 95°, resolidifies, remelts at 164—166°, rearranged at the m.p. or in boiling  $AcOH$  to (I). 2:3:5:6-Tetraphenyl-3a:4- or -3a:7a-dihydroindenone with  $Br-CHCl_3$  gives 4-bromo-2:3:5:6-tetraphenyl-3a:4-dihydroindenone (IV) (84%), m.p. 196° (0.5 active H; adds 1.5  $MgMeI$ ), dehydrogenated by  $Br-CHCl_3$  to 4-bromo-2:3:5:6-tetraphenylindenone (V) (90%), m.p. 234—235°. (V) is reduced by  $Zn-AcOH$  to 4-bromo-2:3:5:6-tetraphenylindanone (57%), m.p. 175°, and with  $MgPhBr$

gives 4-bromo-1-hydroxy-1:2:3:5:6-pentaphenylindenone (52%), m.p. 249°.  $MgPhBr$  and (IV) give (mechanism discussed) 2:3:5:6:7-pentaphenyl-3a:7a-dihydroindenone (27%), m.p. 246° [and a product (20%),  $C_{78}H_{57}O_2Br$ , m.p. 229° (decomp.) (consumes 2.7  $MgMeI$ ; 2 active H)], which with  $MgPhBr$  gives 1-hydroxy-1:2:3:5:6:7-hexaphenyl-3a:7a-dihydroindenone (69%), m.p. 240° (not dehydrated by 2%  $H_2SO_4-AcOH$ ), and with  $HBr$  gives a substance,  $C_{39}H_{27}Br$ , m.p. 194°.  $MgMeI$  and (IV) give 2:3:5:6-tetraphenyl-7-methyl-3a:7a-dihydroindenone (VI) (33%), m.p. 170°, and, in one experiment, 10% of a ketone,  $C_{34}H_{26}O$ , m.p. 217°. (VI) consumes 1  $MgMeI$ , showing 0.3 active H, is unaffected by  $HBr$  or  $(CH \cdot CO)_2O$ , and with Br gives the 7a-Br-derivative (80%), m.p. 239°, whence it is regenerated by  $MgMeI$ . R. S. C.

**Enolisation in the Reformatsky reaction.** M. S. Newman (*J. Amer. Chem. Soc.*, 1942, 64, 2131—2133).—Recovery of ketone after a Reformatsky reaction is due to enolisation and formation of  $CR_2 \cdot CR' \cdot OZnBr$  and  $AlkOAc$ . Thus, acetomesitylene (I) consumes 1 mol. of  $CH_2Br \cdot CO_2Me$  (II) in presence of Zn and  $C_6H_6$  but, after hydrolysis, yields 50% of  $MeOAc$  and 90% of (I);  $MeOAc$  is also obtained by distillation prior to hydrolysis, but in  $\nearrow$  traces by prolonged boiling of (II) and Zn in  $C_6H_6$ . Experiments with 1-keto-2-o-tolyl-3-methyl- and 1-keto-2-phenyl-1:2:3:4-tetrahydronaphthalene and 1-keto-1:2:3:4-tetrahydrophenanthrene (modified prep.) show that (i) for different Br-esters enolisation of the ketone increases in the order  $CH_2Br \cdot CO_2Et < CHMeBr \cdot CO_2Et < CHEtBr \cdot CO_2Et$ ; (ii) use of I to initiate reaction decreases enolisation; (iii) use of dioxan as a solvent promotes enolisation. R. S. C.

**Preparation of 2-keto-1:2:3:4-tetrahydronaphthalene from  $\beta$ -naphthol and analogous transformations.** J. W. Cornforth, (Mrs.) R. H. Cornforth, and (Sir) R. Robinson (*J.C.S.*, 1942, 689—691).—2- $C_{10}H_7 \cdot OMe$  with  $Na-EtOH$  at 115° (bath), followed by immediate hydrolysis (aq.  $HCl$ ), gives 2-keto-1:2:3:4-tetrahydronaphthalene (I) (56%). 1:2- $C_{10}H_6Me \cdot OMe$  similarly affords 2-keto-1-methyl-1:2:3:4-tetrahydronaphthalene (II) (10%), b.p. 137—138°/18 mm. [semicarbazone, m.p. 200—202° (decomp.)], and some 2-methoxy-1-methyl-5:6:7:8-tetrahydronaphthalene, m.p. 51°. 2-Keto-5-methoxy-1:2:3:4-tetrahydronaphthalene (III) (63%), b.p. 120—122°/0.4 mm., is similarly prepared from 1:6- $C_{10}H_8(OMe)_2$ ; the 6- $OMe$ -isomeride is formed by hydrolysis (aq.  $EtOH-HCl$ ) of 2:6-dimethoxy-3:4-dihydronaphthalene (A., 1941, II, 295). Dehydrogenation (S at 220—225°) of 1-keto-6-methoxy-5-methyl-1:2:3:4-tetrahydronaphthalene and methylation ( $Me_2SO_4$ -aq.  $NaOH$ ) of the phenol gives 2:5-dimethoxy-1-methylnaphthalene, m.p. 85°; reduction and hydrolysis then yields 2-keto-5-methoxy-1-methyl-(semicarbazone, m.p. 188—190°) and some 1-keto-6-methoxy-5-methyl-1:2:3:4-tetrahydronaphthalene (2:4-dinitrophenylhydrazones, m.p. 249—250°). Equilenin Me ether when reduced and hydrolysed affords the keto-alcohol (A), m.p. 152—153°,  $[a]_D^{25} + 33.6^\circ$  in  $EtOH$ . The reaction is general only for 2-methoxynaphthalenes; reduction of 2:7-dimethoxyphenanthrene gives only the 9:10- $H_2$ -derivative. (I) and  $MeI-NaOPr^i-Pr^iOH$  (in  $N_2$ ) give (II), whereas (III) similarly yields 2-keto-5-methoxy-1:1-dimethyl-1:2:3:4-tetrahydronaphthalene, m.p. 83—85° (semicarbazone, m.p. 192—194°; 2:4-dinitrophenylhydrazones, m.p. 184°). A. T. P.



**Structure of the bimolecular product formed by the action of acidic dehydrating agents on anhydroacetonebenzil.** C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1942, 64, 2123—2127).—The substance previously (A., 1933, 1164) believed to be 4:7-endo-keto-3:3a:5:6- is now considered to be 4:7-endo-keto-2:3:5:6-tetraphenyl-3a:4:7:7a-tetrahydroindenone (I), the rearrangement,  $>CPh \cdot CPh \cdot CH \rightarrow >CH \cdot CPh \cdot CPh$ , occurring during the formation of (I) from anhydroacetonebenzil [4-hydroxy-3:4-diphenyl- $\Delta^2$ -cyclopentenone]. (I) consumes 2  $MgMeI$ , adding 1 mol. and giving 1  $CH_4$ ; with  $MgRHal$  it gives only (75—85%) monocarbonyls; addition occurs at  $C_{11}$ ; the endo-CO enolises, reacts with  $MgMeI$ , and, after decomp., ketonises. With  $Br-AcOH$  at 100°, (I) gives the 4:7:7a- $Br_3$ -derivative, m.p. 229—230°, converted by  $MgMeI$  into 4:7:7a-tribromo-1-hydroxy-2:3:5:6-tetraphenyl-1-methyl-4:7-endo- $\alpha$ -hydroxyethylidene-3a:4:7:7a-tetrahydroindenone (II), m.p. 278° [consumes 2.7  $MgMeI$ , then regenerates (II)].  $PCl_5$  converts (I) in boiling  $C_6H_6$  into a  $Cl_1$ -derivative, m.p. 215°. By  $MgRHal$  and then standard reactions, (I) gives 1-hydroxy-4:7-endo-keto-2:3:5:6-tetraphenyl-1-methyl-, m.p. 262° [acetates, forms (prep. by  $AcCl$ ), m.p. 202° and (prep. by  $Ac_2O-H_2SO_4$ ), m.p. 180°; derived 1-chloride, m.p. 219°, and 1-bromide, m.p. 191°], -2:3:5:6-tetraphenyl-1- $\alpha$ -naphthyl- (III), m.p. 295° (derived 1-bromide, m.p. 233°), and -1:2:3:5:6-pentaphenyl- (IV), m.p. 226° [acetate (prep. by  $Ac_2O-H_2SO_4$ ), m.p. 235°; derived 1-chloride, m.p. 216°], -3a:4:7:7a-tetrahydroindenone. 2:3:5:6-Tetraphenylindenone and  $MgPhBr$  give 1-hydroxy-1:2:3:5:6-pentaphenylindenone (87%), m.p. 220°, converted by warm  $HBr-AcOH$  into the 1-bromide (89%), m.p. 203°. With Zn dust in boiling  $AcOH$  this gives a hydrocarbon,  $C_{39}H_{28}$ , m.p. 280°, which is also obtained (with evolution of  $CO$  and  $H_2O$ ) from (IV) at 290—310°, a rearrangement

occurring in one or other reaction. (III) gives similarly a hydrocarbon,  $C_{43}H_{30}$ , m.p. 298°. Both oximes (*loc. cit.*) of (I) with boiling EtOH—conc. HCl regenerate (I). Formation of 2-phenylquinoline from  $CHPh:CH:CH:NPh$  (unimol. in boiling EtOH) (Peine, A., 1884, i, 1344) involves a rearrangement analogous to that during the prep. of (I). R. S. C.

**Action of organomagnesium compounds on dianils of  $\alpha\beta$ -diketones. Cyclisation of the  $\alpha$ -anilino ketones obtained.** (Mlle.) M. Garry (*Ann. Chim.*, 1942, [xi], 17, 5—99).—Partly an account of work previously reviewed (A., 1939, II, 376).  $\gamma$ -Anilino- $\beta$ -anilo- $\gamma$ -methylbutane (the  $\alpha$ -anilinoisopropyl ketone anil) (I), m.p. 66° [picrate, m.p. 150° (decomp.)]; Ac derivative, m.p. 242°, is hydrolysed to the ketone (II) [oxime, m.p. 142°, also obtained from (I) and  $NH_2OH$ , or from  $NO\cdot CHMe\cdot CMe_2\cdot O\cdot NO_2$  and  $NH_2Ph$  (cf. Klingstedt, A., 1926, 44); semicarbazone, m.p. 182°; picrate, m.p. 112°; Ac derivative, m.p. 74°; methiodide (III), m.p. 175° (decomp.)], which is reduced by Na—EtOH to  $\gamma$ -anilino- $\gamma$ -methylbutan- $\beta$ -ol, b.p. 149°/17 mm. (N-phenylcarbamyl derivative phenylcarbamate, m.p. 191°; unstable picrate, m.p. 110°). ( $CMe:NPh$ )<sub>2</sub> (IV) with MgMel in boiling  $C_6H_6$  gives  $\beta\gamma$ -dianilino- $\beta\gamma$ -dimethylbutane (V), m.p. 37°, b.p. 216—217°/12 mm. [sulphate, m.p. 190° (decomp.)]; dihydrochloride, m.p. ~190° (decomp.); picrate, m.p. 163°. The anil, m.p. 95° (softens from 82°), b.p. 218—219°/20 mm. (picrate, m.p. 143—144°), of  $\gamma$ -anilino- $\gamma$ -methylpentan- $\beta$ -one (picrate, m.p. 95°) and  $\gamma\delta$ -dianilino- $\gamma\delta$ -dimethylhexane, forms, m.p. 89° and 65° (probably stereoisomerides) [the mixture gives a dihydrochloride, m.p. ~170° (decomp.)], and a monopicrate, m.p. 138° (decomp. from 125°)], are prepared from (IV) and MgEtBr.  $\gamma$ -Anilino- $\beta$ -anilo- $\gamma$ -methylheptane (VI), m.p. 74°, b.p. 225—230°/18 mm. [from (IV) and  $MgBu^aBr\cdot Et_2O$ ], is hydrolysed (aq. HCl) to the ketone (VII), m.p. 86° [picrate, m.p. 130°, also obtained from (VI) and picric acid]. Hydrolysis of the crude reaction product also affords some NHPPhBu and (probably) 2:3-dimethyl-1-butyldiole, b.p. 155—160°/17 mm. (picrate, m.p. 97°).  $MgBu^aBr$  and (IV) in  $C_6H_6$  give  $\epsilon\zeta$ -dianilino- $\epsilon\zeta$ -dimethyldecane [dihydrochloride, m.p. 135° (decomp.)]. (IV) and  $CH_2Ph\cdot MgCl$  afford  $\gamma$ -anilino- $\beta$ -anilo- $\delta$ -phenyl- $\gamma$ -methylbutane, m.p. 100°, and thence the ketone (VIII), m.p. 74°, b.p. 208—210°/16 mm. (picrate, m.p. 125°; oxime, m.p. 178°), reduced to  $\gamma$ -anilino- $\delta$ -phenyl- $\gamma$ -methylbutan- $\beta$ -ol, b.p. 213°/14 mm. Ph  $\alpha$ -anilino- $\alpha$ -phenylethyl ketone (IX), m.p. 142° (hydrochloride, m.p. 138—142°; picrate, m.p. 168°), is not obtained (cf. Cameron, A., 1930, 345) from Ph  $\alpha$ -chloro- $\alpha$ -phenylethyl ketone, m.p. 57—58° (from  $COPh\cdot CPhMe\cdot OH$  and  $SOCl_2$ ), and  $NH_2Ph$ , whereby (probably) Ph  $\alpha$ -phenylvinyl ketone, m.p. 52—57°, results. ( $CPh:NPh$ )<sub>2</sub> and MgEtI give  $\beta$ -anilino- $\alpha$ -anilo- $\alpha\beta$ -diphenylbutane, m.p. 183.5° (free ketone, m.p. 143°), with (mainly)  $COPh\cdot CPh:NPh$ ,  $NH_2Ph$ , NHPPhEt,  $Bz_2$ , NHPPhBz, and  $BzOH$ . Absorption spectra of many of the compounds are shown. (II) with  $NH_2Ph$  (excess) and  $NH_2Ph\cdot HCl$  at 180°, with a little  $NH_2Ph\cdot HCl$  at 180°, or with  $ZnCl_2$  at 140°, gives 2:3:3-trimethylindolenine, b.p. 110°/10 mm. [picrate, m.p. 155°; methiodide, also obtained by heating (III)], also prepared from (II) by heating with a little  $Na_2SO_4$  or  $NH_2Ph\cdot HCl$ . NHPPh- $CMeEt\cdot COMe$  similarly yields 2:3-dimethyl-3-ethylindolenine, b.p. 128°/22 mm., and (VII) with a little  $NH_2Ph\cdot HCl$  at 180° affords 2:3-dimethyl-3-butyldiole, b.p. 142—143°/17 mm. (picrate, m.p. 137°; methiodide, m.p. 211°). (VIII) with  $NH_2Ph + NH_2Ph\cdot HCl$  at 175—180° gives 2:3-dimethylindole and a little  $CH_2Ph\cdot NHPPh$ , but with  $ZnCl_2$  at 180° affords 3-benzyl-2:3-dimethylindolenine, b.p. 188—190°/18 mm. (picrate, m.p. 139°). (IX) and  $NH_2Ph + NH_2Ph\cdot HCl$  at 160—165° yield one or other of the isomerides, 2:3-diphenyl-3- (X), m.p. 108° (no reaction with  $Ac_2O$ ; picrate, m.p. 155°), or 3:3-diphenyl-2-methylindolenine (XI), m.p. 145° (picrate, m.p. 210°); (XI) is usually formed and conditions for preparing (X) are not established. The methiodide, m.p. 188°, of (X) is converted by  $NaOH\cdot EtOH$  into (probably) 2-hydroxy-2:3-diphenyl-1:3-dimethylindoline, m.p. 110°, whereas the methiodide, m.p. 230°, of (XI) and aq.  $NaOH$  in  $Et_2O$  give 3:3-diphenyl-1-methyl-2-methyleneindoline, m.p. 101° (picrate, m.p. 178°). With  $Ac_2O\cdot NaOAc$ , (XI) affords 1-acetyl-3:3-diphenyl-2-methyleneindoline, m.p. 138°. Cyclisation of (IX) to (XI) is effected by a little  $NH_2Ph\cdot HCl$  at 170—180°, or by heating its hydrochloride to 190°. (X) is synthesised from  $Mg$  2:3-diphenylindolyl iodide and  $MeI$  in  $PhMe$  at 90°, or from the phenylhydrazone, m.p. 129—131°, of  $COPh\cdot CHPhMe$  and aq.  $HCl$ . A. T. P.

**Action of alkaline reagents on the bimolecular product formed by the action of acidic dehydrating agents on anhydroacetonebenzil.**

F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1942, 64, 2120—2123).—4:7-endoKeto-2:3:5:6-tetraphenyl-3a:4:7:7a-tetrahydroindenone (modified prep.; 90% yield) with boiling  $KOH\cdot EtOH$  gives 2:3:5:6-tetraphenyl-3a:4:7:7a-tetrahydroindenone-7-carboxylic acid (I) (76%), m.p. 275—276° (no  $CO$  evolved) (anilide, m.p. 269°) (cf. A., 1933, 1164; 1937, II, 457).  $NaOMe$  or  $NaOEt$  gives similarly the *Me*, m.p. 193° [also obtained from (I) by  $CH_2N_2$ ], and *Et* ester, m.p. 159—160° (with some acid), respectively, of (I). The esters are stable to  $KMnO_4\cdot COMe_2$ , but (I) with  $KMnO_4\cdot aq. K_2CO_3$  at 85—95° gives, by loss of  $HCO_2H$ , 2:3:5:6-tetraphenyl-3a:4-dihydroindenone (II) (56%), m.p. 239—240°, which is also obtained from 2:3:5:6-tetraphenyl-3a:7a-dihydroindenone (III) (modified prep.; 70—75% yield; cf. *loc. cit.*)

by  $HBr\cdot AcOH$  at 100° or  $H_2SO_4\cdot AcOH$ . (II) does not add  $(CH_3CO)_2O$ , adds 1  $MgMel$  (no gas), and at 300° is isomerised to 2:3:5:6-tetraphenylindanone (IV). With  $MgPhBr\cdot Et_2O$  at room temp., followed by aq.  $NH_4Cl$ , (II) gives, by 1:2- and 1:4-addition, respectively, 1-hydroxy-1:2:3:5:6-pentaphenyl-3a:4-dihydroindenone (V) (25%), m.p. 233°, and 2:3:5:6:7-pentaphenyl-3a:4:7:7a-tetrahydroindenone (VI) (60%), forms, m.p. 178—179° and 145—146°; when dil. acid replaces the  $NH_4Cl$ , a hydrocarbon,  $C_{39}H_{28}$  (VII), m.p. 222°, which does not add  $(CH_3CO)_2O$ , is isolated instead of (V). These results prove the structure of (I). With  $MgPhBr$  and then aq.  $NH_4Cl$ , (IV) gives 1-hydroxy-1:2:3:5:6-pentaphenylindane, m.p. 228—229° (decomp.), and thence ( $H_2SO_4\cdot AcOH$ ) (VII); (III) gives similarly a glassy carbinol and then (VII). (VI) exists partly as the enol, since with  $AcCl$  it gives an acetate (70%), m.p. 115° [consumes 2  $MgMel$  without evolution of gas; subsequent hydrolysis regenerates (VI)], and with  $MgMel$  gives 0.67  $CH_4$ ; it gives no oxime, does not react with  $(CH_3CO)_2O$ , and with  $Br\cdot CHCl_3$  affords the 7a-*Br*-derivative, anhyd., m.p. 218—219°, and  $+C_6H_6$ , softens at ~144°, m.p. 234° [whence (VI) is regenerated by  $MgMel$  (1 mol. consumed; no  $CH_4$  evolved)], which is unaffected by  $C_6H_5N$ ,  $KOAc$ ,  $HBr$ ,  $AcCl$ , or  $Br$ . Some of the above reactions necessitate allylic rearrangements. R. S. C.

**Decahydronaphthalene-1:5-dione and 2:2'-diketodicyclopentyl.**

B. J. F. Hudson and (Sir) R. Robinson (*J.C.S.*, 1942, 691—693).—Et  $\alpha$ -bromoadipate and Ag powder at 140—160° give Et<sub>4</sub> octane- $\alpha\delta\epsilon\theta$ -tetracarboxylate, b.p. 192—195°/0.2—0.3 mm., converted by K (not Na) in  $PhMe$  at room temp., followed by hydrolysis with aq.  $EtOH\cdot HCl$ , into 2:2'-diketodicyclopentyl (I), m.p. 67—69° [bis-2:4-dinitrophenylhydrazones, m.p. 230—240° (decomp.)], contaminated with (probably) (III) (below). Methylation ( $NaNH_2\cdot MeI\cdot Et_2O$ ) of (I) gives a *Me*<sub>1</sub> derivative, b.p. 175—185°/14 mm. [di-oxime, m.p. 207—211° (decomp.)]. (I) is prepared (2—4% yield) in a purer form by hydrolysis (aq.  $NaOH\cdot EtOH$ ) of the product from Et sodiocyclopentanone-2-carboxylate and I in  $Et_2O$ . Hydrogenation (Raney Ni in  $EtOH$ ) of 1:5- $C_{10}H_8(OH)_2$  at 150—200°/120 atm. gives mixed decahydro- $\alpha$ -naphthols (*cis*-form, m.p. 92—94°, isolated) and 5—8% of x-decahydronaphthalene-1:5-diol (II), m.p. 130—150° [a form, m.p. 159—161°, probably a stereoisomeride of that described by Campbell *et al.* (A., 1942, II, 90), is described]. Use of Cu chromite as catalyst gives mainly phenolic products; 5:6:7:8-tetrahydro-1-naphthol, m.p. 65°, and a substance, m.p. 165—170° (acetate, m.p. 129—131°), are isolated. (II) and  $CrO_3\cdot aq. AcOH$  at 0° to room temp. yield 10% of decahydronaphthalene-1:5-dione (III) (probably *trans*), m.p. 165—167° [bisphenylhydrazones (IV), m.p. 230°], or a mixture of (III) and the *cis*-form, m.p. 68—72° [bisphenylhydrazones (V), m.p. 172—173° to a gum, becoming clear at 208—210°]; mixtures are converted into (III) by  $AcOH$  at 100° (6 hr.). (V) and aq.  $HCl$  or  $EtOH\cdot HCl$  yield 3:4:7:8:9:10-hexahydronaphthalene-1:2:5:6-bis-(2:3)-indole, m.p. 312—316° (decomp.); (IV) similarly yields a substance, m.p. 292—296° (decomp.). A. T. P.

**Homogeneous catalysis and solvent effects in or diene synthesis.**—See A., 1943, I, 21.

**Alkylation of 1:4-naphthaquinones with esters of quadrivalent lead.** L. F. Fieser and F. C. Chang (*J. Amer. Chem. Soc.*, 1942, 64, 2043—2052).— $Pb(OAc)_4$  in boiling  $AcOH$  introduces *Me* adjacent to a  $CO$  of 1:4-naphthaquinone or its alkyl derivatives, the reaction being much accelerated by presence of a promoter, *e.g.*,  $CH_2(CO_2H)_2$ ,  $MeOH$ , etc. (cf. below). 2-Methyl-5:8-dihydro-1:4-naphthaquinol (I) etc. promotes its own methylation. Use of  $RCO_2H$ , a promoter, and an excess of  $Pb_2O_3$  leads to introduction of R. (I) (improved prep.) or the derived  $H_2$ -quinone with  $Pb(OAc)_4$  in boiling  $AcOH$  gives 2:3-dimethyl-1:4-naphthaquinone (II) (up to 28%) (quinol diacetate, m.p. 190—190.5°). 2-Methyl-1:4-naphthaquinone (III) is slowly affected by this treatment, but is rapidly converted into (II) if interaction occurs in presence of  $CH_2(CO_2H)_2$  (49% yield),  $CHMe(CO_2H)_2$ ,  $CH_2Ac\cdot CO_2Et$ ,  $CH_2EtAc\cdot CO_2Et$  (46% yield),  $MeOH$ , or tartronic acid, but  $CMe_2(CO_2H)_2$ ,  $CH_2(CO_2Et)_2$ ,  $CHPh_3$ , cyclopentadiene, and acenaphthene are ineffective. *o*-Xyloquinone and  $(CH_2)_2CMe_2$  in boiling  $EtOH$  give 2:3:6:7-tetramethyl-5:8:9:10-tetrahydro-1:4-naphthaquinone, m.p. 105—106.5°, isomerising to 2:3:6:7-tetramethyl-5:8-dihydro-1:4-naphthaquinol, m.p. 269—270.5° (lit. 232°), oxidised by  $CrO_3$  or  $Pb(OAc)_4$  to 2:3:6:7-tetramethyl-1:4-naphthaquinone, m.p. 169.5—170° (lit. 167—168°) (quinol diacetate, m.p. 216—217°), which is also obtained from 2:6:7-trimethyl-5:8-dihydro-1:4-naphthaquinol by  $Pb(OAc)_4$  in boiling  $AcOH$ . 2-Methyl-3-ethyl-1:4-naphthaquinone, m.p. 72—72.6° (quinol diacetate, m.p. 106—108°, resolidifies, remelts at 116—117°), is obtained from (III) by  $EtCO_2H$ ,  $Pb_2O_3$ , and  $CH_2Ac\cdot CO_2Et$  at 100° or from 1:2:4- $O\cdot C_{10}H_5Et\cdot O$  by  $Pb(OAc)_4\cdot AcOH\cdot CH_2(CO_2H)_2$ . With  $RCO_2H$ ,  $Pb_2O_3$ , and a promoter at 100° to 120—130° (III) gives similarly 2-methyl-3-n- (IV) (47%), m.p. 65—65.4°, sublimes at 53—58°/1 mm. (quinol diacetate, m.p. 93.5—95°), and -3-iso-propyl- (V) (59%), m.p. 110—111.2° (quinol diacetate, m.p. 115—116°), -3-n-heptyl- (34%), m.p. 80.4—80.8°, sublimes at 70—76°/1 mm. (quinol diacetate, m.p. 64—65°), -3-benzyl- (65% crude), m.p. 108—108.5°, sublimes at 80°/1 mm. (quinol diacetate, m.p. 163—164.5°), and -3- $\beta$ -phenylethyl- (14.5%), m.p. 73—73.5°

(quinol diacetate, m.p. 140.5—141.2°), -1:4-naphthaquinone. 1:2:4-O:C<sub>10</sub>H<sub>5</sub>Pr<sup>a</sup>:O, m.p. 40.5—41° (lit. 39—39.5°), with Pb(OAc)<sub>4</sub> and CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> in boiling AcOH (not at 100°) gives (IV). β-Naphthylidimethylcarbinol (prep. from 2-C<sub>10</sub>H<sub>7</sub>·COME by MgMeI), m.p. 65—65.5°, could not be reduced. 2-C<sub>10</sub>H<sub>7</sub>Pr<sup>β</sup> (prep. by a Friedel-Crafts reaction; 14% yield) with CrO<sub>3</sub> gives 1:2:4-O:C<sub>10</sub>H<sub>5</sub>Pr<sup>β</sup>:O, an oil, which with Pb(OAc)<sub>4</sub>·CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub>·AcOH gives (V). M.p. are corr. R. S. C.

**Alkylation of p-quinones by acyl peroxides.** L. F. Fieser and A. E. Oxford (*J. Amer. Chem. Soc.*, 1942, **64**, 2060—2065).—Interaction of 1:2:4-O:C<sub>10</sub>H<sub>5</sub>Me:O (I) with Pb(OAc)<sub>4</sub> (excess) in AcOH at 90—100° is promoted by MeOH, H<sub>2</sub>O, Pr<sup>β</sup>OH, Bu<sup>γ</sup>OH (induction period), Pr<sup>β</sup>2O, C<sub>6</sub>H<sub>6</sub>, PhMe, cyclohexane (II), and n-C<sub>8</sub>H<sub>18</sub>, the products being 1:2:3:4-O:C<sub>10</sub>H<sub>4</sub>Me<sub>2</sub>:O, CO<sub>2</sub>, and (?) C<sub>2</sub>H<sub>6</sub>. In absence of (I), all the promoters except Bu<sup>γ</sup>OH cause decomp. of Pb(OAc)<sub>4</sub> in AcOH, relative efficiencies being C<sub>6</sub>H<sub>6</sub> > (II) > C<sub>8</sub>H<sub>18</sub> > PhMe. The (II) is largely unchanged; the decomp. of Pb(OAc)<sub>4</sub> eventually ceases but is restarted by adding more (II); Pb(OAc)<sub>4</sub> is unchanged in (II) alone and then does not methylate (I); Pb(OAc)<sub>2</sub> formed may be partly responsible, since it retards the reaction of (I) with Pb(OAc)<sub>4</sub> in AcOH-PhMe-(II). Diacyl peroxides (best, 1 mol.) in AcOH at 90° alkylate many quinones, no promoter being required; the acyl may be unsaturated; the reacting quinone may be substituted by a lower alkyl, Br, or OH, but not by OMe or higher alkyl; aroyl and aracyl peroxides are consumed but give no or indefinite products. Thus are prepared: from (I), 2-methyl-3-pentadecyl- (60%), m.p. 95—97°, -3-heptadecyl- (60%), m.p. 96°, -3-Δ<sup>4</sup>-heneicosenyl- (? mixed isomerides) (small yield), m.p. 39—81°, -3-norchaulmoogryl- (40%), softens at 57°, m.p. 65—68°, -3-Δ<sup>4</sup>-decenyl- (40%), m.p. 68°, and -3-Δ<sup>4</sup>-hexadecenyl- (25%), m.p. 72—73°, -1:4-naphthaquinone; phthiocol (50%) from 1:2:4-O:C<sub>10</sub>H<sub>5</sub>(OH):O; 2-pentadecyl-1:4-naphthaquinone (small yield), m.p. 71—72°, from 1:4-O:C<sub>10</sub>H<sub>6</sub>:O; duroquinone (small yield) and 2:3:5-trimethyl-6-pentadecyl-1:4-benzoquinone (25%), m.p. 74°, from 1:2:3:5:4-O:C<sub>6</sub>HMe<sub>3</sub>:O; 1:2:3:5:4-O:C<sub>6</sub>HMe(OMe)<sub>2</sub>:O from 1:2:6:4-O:C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>:O; 1:3:6:2:5:4-O:C<sub>6</sub>Ph<sub>2</sub>(OH)<sub>2</sub>:O (very little) and 2:5-dihydroxy-3-pentadecyl-1:4-benzoquinone (small yield), m.p. 136—138°, from 1:2:5:4-O:C<sub>6</sub>H<sub>2</sub>(OH)<sub>2</sub>:O; 1:2:3:5:6:4-O:C<sub>6</sub>MeBr<sub>3</sub>:O (with H<sub>2</sub>-Pd-BaSO<sub>4</sub>-NaOAc gives toluquinol) (68%) from 1:2:3:5:4-O:C<sub>6</sub>HBr<sub>3</sub>:O. R. S. C.

**Celastrol. Spectrographic characterisation and colour tests.** L. F. Fieser and R. N. Jones (*J. Amer. Pharm. Assoc.*, 1942, **31**, 315—317).—The ultra-violet absorption spectra of celastrol (I) and methylcelastrol indicate β-naphthaquinonoid structures. Colour reactions with aq. EtOH-NaHSO<sub>3</sub>, boroacetic anhydride, and CN·CH<sub>2</sub>·CO<sub>2</sub>Et-NH<sub>3</sub>-EtOH indicate that (I) is an 8-hydroxy-3:4-dialkyl-1:2-naphthaquinone and may be the 2-methyl-3-hydrogeranyl (or homohydrogeranyl) derivative. F. O. H.

**"Naphthylidenesulphanilamide" derivatives.** F. Irreverre and M. X. Sullivan (*J. Amer. Chem. Soc.*, 1942, **64**, 2230—2231).—Treating p-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH<sub>2</sub> (I) in H<sub>2</sub>O with 1:4:2-O:C<sub>10</sub>H<sub>5</sub>(SO<sub>3</sub>Na):O at ~50—60° (later 0°) gives 3-hydroxy-1:4-naphthaquinone-1-p-sulphamylaniol, m.p. 271—273°; (I) with, successively, 1:4:6:2-O:C<sub>10</sub>H<sub>4</sub>(SO<sub>3</sub>Na)<sub>2</sub>:O, H<sub>2</sub>O<sub>2</sub>, and NaCl at room temp. (later 0°) gives Na 3-hydroxy-1:4-naphthaquinone-1-p-sulphamylaniol-7-sulphonate, and with 1:2:4-O:C<sub>10</sub>H<sub>5</sub>(SO<sub>3</sub>K):O at ~70° and then HCl at 30° (later cooling at 0°) gives 3-p-sulphamylaniolino-2-sulpho-1:4-naphthaquinone-1-p-sulphamylaniol, m.p. 276—278°. R. S. C.

**Naphtol AS series. VII. Synthetic experiments. IV. 2-Hydroxy-3-naphthoyl derivatives of aminoanthraquinones.** R. V. Bhat, (Miss) K. D. Gavankar, and K. Venkataraman (*J. Indian Chem. Soc., Ind. Ed.*, 1942, **5**, 171—177; cf. A., 1942, II, 405).—1:2'-Hydroxy-3'-naphthoylaminoanthraquinone, m.p. 240—241° (acetate, m.p. 261—262°; benzoate, m.p. 225—226°; p-toluenesulphonate, m.p. 288—289°), is prepared from 1-aminoanthraquinone (I) and 2:3-OH·C<sub>10</sub>H<sub>6</sub>·COCl in boiling PhNO<sub>2</sub>. 1:4-Diaminoanthraquinone similarly affords 1:4-di-(2'-hydroxy-3'-naphthoylamino)anthraquinone, m.p. 290—291° [diacetate, m.p. 285—286° (decomp.); dibenzoate, m.p. 249—250°; di-p-toluenesulphonate, m.p. 225—226°], but 1:5-diaminoanthraquinone similarly yields 1-amino-5-(2'-hydroxy-3'-naphthoylamino)anthraquinone, m.p. 278—279° [Ac<sub>2</sub> derivative, m.p. 325° (decomp.)], insol. in NaOH-EtOH at 60°. 1-p-Nitrobenzamidoanthraquinone, m.p. 280—281° [from (I) and p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·COCl in PhCl at 150°], is reduced by Fe and a little AcOH to the NH<sub>2</sub>-derivative, m.p. 336—337°, converted into 1-p-2'-hydroxy-3'-naphthoylaminoanthraquinone, m.p. 349—350°. Clear solutions are not obtained with the compounds and aq. alkali. Dyeing trials (as vat dyes; also after development) are recorded. A. T. P.

#### IV.—STEROLS AND STEROID SAPOGENINS.

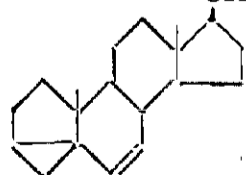
**Recovery of sterols.**—See B., 1943, III, 21.

**Beech bark (*Fagus silvatica*). III.** E. Clotofski and W. Herr (*Ber.*, 1942, **75**, [B], 237—243).—Extraction with light petroleum

and concn. of the extract causes the separation of a mixture of isomeric fatty alcohols and paraffins, a compound (I), m.p. 290—292°, [α]<sub>D</sub><sup>25</sup> +56.3° in CHCl<sub>3</sub>, and a sterol (II) isolated by pptn. with digitonin and also obtained with arachidic and resin acid from the light petroleum mother-liquors. (I) gives the Salkowski and Liebermann-Burchard reactions. It could not be recovered unchanged by hydrolysis of the acetate, m.p. 271°, formate, m.p. 181°, or benzoate, m.p. 118—122°. It is hydrolysed by C<sub>5</sub>H<sub>11</sub>·OH-HCl to a compound, C<sub>29</sub>H<sub>48</sub>O<sub>2</sub>, m.p. 232° (diacetate, m.p. 273°), which is neutral and does not contain :CO; a sugar residue is not removed by hydrolysis. (II), C<sub>24</sub>H<sub>40</sub>O (+EtOH), m.p. 134°, [α]<sub>D</sub><sup>25</sup> -31.25° in CHCl<sub>3</sub>, is identical with the sterol isolated by Zellner (A., 1926, 1281) but not with stigmaterol. The acetate (III), m.p. 121—122°, [α]<sub>D</sub><sup>25</sup> -32.4° in CHCl<sub>3</sub>, dibromoacetate, m.p. 123—124°, benzoate, m.p. 141.5°, p-nitrobenzoate, m.p. 187°, and allophanate, m.p. 258°, are described. Oxidation of (II) by Al(OBu<sup>γ</sup>)<sub>3</sub> in COMe<sub>2</sub>-C<sub>6</sub>H<sub>6</sub> affords the ketone, C<sub>24</sub>H<sub>38</sub>O, m.p. 103°; the corresponding semicarbazone, m.p. 248° (decomp.), is reduced (Wolff-Kishner) to the hydrocarbon, C<sub>24</sub>H<sub>40</sub>, m.p. 77—78°. Hydrogenation [Pd-C in Et<sub>2</sub>O-AcOH (1:1)] yields the dihydrosteryl acetate, m.p. 130.5°, hydrolysed to the dihydrosterol, m.p. 138°. The presence of one double linking is confirmed by titration with Br. H. W.

**Chemical behaviour of cafesterol.** P. N. Chakravorty and M. M. Wesner (*J. Amer. Chem. Soc.*, 1942, **64**, 2235).—Data in the literature (Wettstein, A., 1942, II, 198, 371; Slotta *et al.*, A., 1939, II, 18) are corr. Cafesterol (I) does not contain an aromatic ring, since with HNO<sub>3</sub> it gives only a non-acidic NO<sub>2</sub>-compound, m.p. 220—230°. It contains reactive, conjugated ethylenic linkings: with (:CH·CO)<sub>2</sub>O in C<sub>6</sub>H<sub>6</sub> at room temp. or slightly warm it gives an adduct, m.p. 185—192°, but decomp. occurs in boiling C<sub>6</sub>H<sub>6</sub>. In EtOH it absorbs 2 H<sub>2</sub> (20% Pd-C), giving a H<sub>2</sub>-derivative, m.p. 153—155°; this and its acetate, m.p. 150—152°, give no colour with conc. HCl in EtOH. Na-EtOH or -C<sub>5</sub>H<sub>11</sub>·OH reduces (I) to a product, m.p. 153—156° (with conc. HCl-EtOH gives a stable purple colour) [acetate, m.p. 162—165° (yellow-orange colour with HCl), which with (:CH·CO)<sub>2</sub>O gives an adduct, m.p. 185° (no colour with HCl)]. No details are given. R. S. C.

**Preparation and dehydration of diphenyl-6-methoxy-i-norcholenylcarbinol.** B. Riegel, M. F. W. Dunker, and McC. J. Thomas (*J. Amer. Chem. Soc.*, 1942, **64**, 2115—2120).—Me 6(a)-methoxy-i-cholenate (prep. from Me 3-p-toluenesulphonyloxy-Δ<sup>5</sup>-cholenate and KOAc-MeOH), a syrup, [α]<sub>D</sub><sup>21</sup> +44.1° in CHCl<sub>3</sub>, with MgPhBr-Et<sub>2</sub>O and then aq. NH<sub>4</sub>Cl gives diphenyl-6(a)-methoxy-i-norcholenylcarbinol (I), m.p. 139—140.2°, [α]<sub>D</sub><sup>27</sup> +43.9° in CHCl<sub>3</sub>. Me 3-hydroxy-Δ<sup>5</sup>-cholenate with an excess of MgPhBr gives diphenyl-3-hydroxy-Δ<sup>5</sup>-norcholenylcarbinol (II), softens at 95°, melts (effervescence; ? dehydration), resolidifies at 108°, remelts at 169.4—172.2° [3-p-toluenesulphonate (III), m.p. 143.2—144° or (? loss of H<sub>2</sub>O) m.p. 62°, resolidifies, remelts at 136—137°]. KOAc-MeOH converts (III) into (I). (II) or its 3-acetate (prep. by Ac<sub>2</sub>O-C<sub>5</sub>H<sub>5</sub>N), m.p. 163.2—165.5° (lit. 172—172.5°), in boiling Ac<sub>2</sub>O-AcOH or AcOH gives 3-acetoxy-24:24-diphenyl-Δ<sup>5:23</sup>-choladiene (IV), m.p. 166.6—167.4°, also obtained from (I) by boiling AcOH. Hydrolysis of (IV) by boiling NaOPr<sup>a</sup>-Pr<sup>a</sup>OH (later addition of H<sub>2</sub>O) or by activated Al<sub>2</sub>O<sub>3</sub> in boiling xylene gives 3-hydroxy-24:24-diphenyl-Δ<sup>5:23</sup>-choladiene, m.p. 173—174°, the 3-p-toluenesulphonate, m.p. 130.6—131.5°, of which with KOAc-MeOH gives aa-diphenyl-β-6(a)-methoxy-i-bisnorcholenylethylene (V), m.p. 109.1—110.1°, [α]<sub>D</sub><sup>25</sup> +67.8° in CHCl<sub>3</sub> [with Ac<sub>2</sub>O-AcOH gives (IV)]. With I in boiling xylene, (I) gives (?) diphenyl-3-iodo-Δ<sup>5</sup>-norcholenylcarbinol, m.p. 168.2—169.4°. Activated Al<sub>2</sub>O<sub>3</sub> and (I) in boiling xylene give (?) aa-diphenyl-β-6(β)-methoxy-i-bisnorcholenylethylene (VI), m.p. 161.8—163°, [α]<sub>D</sub><sup>20</sup> -38.6±2° in CHCl<sub>3</sub> [with Ac<sub>2</sub>O-AcOH gives (IV)]. Me 3-methoxy-Δ<sup>5</sup>-cholenate (prep. from the 3-p-toluenesulphonate by boiling MeOH), m.p. 109.2—109.6°, [α]<sub>D</sub><sup>23</sup> -44.6° in CHCl<sub>3</sub>, with MgPhBr (excess) gives diphenyl-3-methoxy-Δ<sup>5</sup>-norcholenylcarbinol, m.p. 164.8—165.9°, dehydrated by boiling AcOH to 3-methoxy-24:24-diphenyl-Δ<sup>5:23</sup>-choladiene, m.p. 114.5—115.3°, [α]<sub>D</sub><sup>24</sup> -11.55±0.66° in CHCl<sub>3</sub>, which is also obtained from (V) or (VI) by boiling H<sub>2</sub>SO<sub>4</sub>-MeOH. With activated Al<sub>2</sub>O<sub>3</sub> in boiling xylene, (V) gives a hydrocarbon (? VII), m.p. 162—163°, [α]<sub>D</sub><sup>25</sup> -18.5° in CHCl<sub>3</sub>, converted into (IV) by boiling AcOH. M.p. are corr. R. S. C.



(VII)

**Marine products. XII. Oxidation of poriferasterol.** A. M. Lyon and W. Bergmann (*J. Org. Chem.*, 1942, **7**, 428—431).—Poriferasterol is oxidised by Al(OPr<sup>β</sup>)<sub>3</sub> in boiling PhMe-cyclohexanone to poriferastrenone, m.p. 111—112.5°, [α]<sub>D</sub><sup>25</sup> +56.7° (2:4-dinitrophenylhydrazones, m.p. 231.8—234.5°; semicarbazone, m.p. 229—230°). Treatment of poriferasteryl acetate (I) with 1 mol. proportion of Br and then with O<sub>3</sub> gives 3(β)-hydroxybisnorcholenic acid, m.p. 291—292° (decomp.) [Me ester, m.p. 140—141° (acetate, m.p. 137.5°)]. Ozonisation of (I) gives a C<sub>7</sub> fragment isolated as the 2:4-dinitrophenylhydrazone, C<sub>13</sub>H<sub>18</sub>O<sub>4</sub>N<sub>4</sub>, m.p. 113—114°, [α]<sub>D</sub><sup>25</sup> ±0°

Clionasterol is shown to be 22 : 23-dihydroporiferasterol. M.p. are corr. H. W.

**Derivatives of œstrone containing oxygen at C<sub>(14)</sub>.** M. N. Huffman (*J. Amer. Chem. Soc.*, 1942, **64**, 2235—2236).—16-Oximino-œstrone (I) and Zn in AcOH give mixed  $\alpha$ -ketols (A), including a 16-hydroxy-œstrone, m.p. 234—237°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -102° in EtOH [benzoate, m.p. 241.5—243.5°; oxime, m.p. 222.5—223°; Me ether, m.p. 174—177° (oxime, m.p. 175—177°)]; H<sub>2</sub>-PtO<sub>2</sub> reduces (A) to mixed triols, including an œstriol, m.p. 267—269°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +88° in EtOH (Me ether, m.p. 141—142°; triacetate, m.p. 152°). Œstrone Me ether gives mixed  $\alpha$ -ketols, oxidised by Cu(OAc)<sub>2</sub> to 16-keto-œstrone Me ether, m.p. 176—178°, the dioxime, m.p. 230°, of which is also obtained from the Me ether of (I) and NH<sub>2</sub>OH. 16-Keto-œstrone-dioxime, m.p. 230—231°, with Cu(OAc)<sub>2</sub>-EtOH gives a highly coloured Cu complex, sol. in CHCl<sub>3</sub>, but no coloured Ni or Co complex. No details are given. R. S. C.

**Sterols. CLI. Rearrangement of 17 : 21-dibromoallopregnan-3( $\beta$ )-ol-20-one acetate.** R. E. Marker, H. M. Crooks, jun., R. B. Wagner, and E. L. Wittbecker. **CLII. Rearrangement of 16 : 17-dibromopregnan-3( $\beta$ )-ol-20-one.** R. E. Marker, R. B. Wagner, and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1942, **64**, 2089—2092, 2093—2097).—CLI. allopregnan-3( $\beta$ )-ol-20-one (I) and Br (1 mol.) in AcOH at room temp. give the 17-Br-derivative (II), m.p. 93—96°, which with Fe dust in AcOH at 100° or H<sub>2</sub>-Pd-BaSO<sub>4</sub> in C<sub>5</sub>H<sub>5</sub>N-dioxan at 40 lb. regenerates (I) and with boiling C<sub>5</sub>H<sub>5</sub>N gives  $\Delta^{16}$ -allopregnen-3( $\beta$ )-ol-20-one. 3( $\beta$ )-Acetoxyallopregnan-20-one (III) gives similarly 17-bromo-3( $\beta$ )-acetoxyallopregnan-20-one (IV), m.p. 155°, converted into (III) by H<sub>2</sub>-Pd-BaSO<sub>4</sub> in MeOH-dioxan-C<sub>5</sub>H<sub>5</sub>N at 40 lb. and by boiling C<sub>5</sub>H<sub>5</sub>N into 3( $\beta$ )-acetoxy- $\Delta^{16}$ -allopregnen-20-one [with Zn dust in AcOH gives (III)]. CrO<sub>3</sub>-AcOH at room temp. oxidises (II) to a mixture, which with boiling C<sub>5</sub>H<sub>5</sub>N or KOAc-AcOH gives  $\Delta^{16}$ -allopregnene-3 : 20-dione (V) and with Fe dust in AcOH at 100° gives allopregnane-3 : 20-dione [obtained from (V) by Zn dust in AcOH at 100°]. 2 mols. of Br with (III) or 1 mol. with (IV) in AcOH at 40° gives 17 : 21-dibromo-3( $\beta$ )-acetoxyallopregnan-20-one, m.p. 174°, converted by boiling KOH-MeOH into 3( $\beta$ )-hydroxy- $\Delta^{17(20)}$ -allopregnen-21-oic acid (VI), m.p. 249°. The derived OAc-acid with O<sub>3</sub>-CHCl<sub>3</sub> and then hot KOH-MeOH gives isoandrosterone (isolated as semicarbazone). Oxidation of (VI) by Al(OBu<sup>t</sup>)<sub>3</sub>-COMe<sub>2</sub>-C<sub>6</sub>H<sub>6</sub> and then reduction by Al(OPr<sup>i</sup>)<sub>3</sub>-Pr<sup>i</sup>OH gives 3( $\alpha$ )-hydroxy- $\Delta^{17(20)}$ -allopregnen-21-oic acid, m.p. 232—235°, converted by O<sub>3</sub>-CHCl<sub>3</sub> etc. into androsterone. cycloHexyl Me ketone with Br at 0° and then KOH-EtOH at room temp. gives cyclohexylideneacetic acid.

CLII. 3( $\beta$ )-Acetoxy- $\Delta^{16}$ -pregnen-20-one with Br-AcOH gives the dibromide, m.p. 137—140°, whence it is regenerated by H<sub>2</sub>-Pd-BaSO<sub>4</sub> in C<sub>5</sub>H<sub>5</sub>N-dioxan at 3 atm., boiling C<sub>5</sub>H<sub>5</sub>N, NaI-MeOH, or KOAc-AcOH, and which with boiling KOH-MeOH gives 3( $\beta$ )-hydroxy- $\Delta^{17(20)}$ -pregnen-21-oic acid (VII), m.p. 254—256° (decomp.) (acetate, m.p. 161—163°), and its Me ester (VIII), m.p. 153—156° [acetate (IX), m.p. 103—105°; also prepared from (VII) by CH<sub>2</sub>N<sub>2</sub>]. H<sub>2</sub>-PtO<sub>2</sub> at 3 atm. reduces (VII) to 3( $\beta$ )-hydroxypregnan-21-oic acid (X) {acetate; Me ester (XI), m.p. 141—143° [acetate (XII), m.p. 105—106°]} and (IX) to (XII). With O<sub>3</sub>-CHCl<sub>3</sub> or KMnO<sub>4</sub>-KOH at 0°, (VII) gives ætiocholan-3( $\beta$ )-ol-20-one. With, successively, Al(OPr<sup>i</sup>)<sub>3</sub>-COMe<sub>2</sub>-PhMe, Al(OPr<sup>i</sup>)<sub>3</sub>-Pr<sup>i</sup>OH, removal of precipitable material by digitonin, and O<sub>3</sub>-CHCl<sub>3</sub>, (VIII) gives ætiocholan-3( $\alpha$ )-ol-17-one. Na-n-C<sub>5</sub>H<sub>11</sub>-OH and then KOH-MeOH converts (VII) or (X) into 3( $\alpha$ )-hydroxypregnan-21-oic acid, m.p. 224—226° [Me ester, m.p. 118—119° (acetate, m.p. 85—87°)], oxidised by CrO<sub>3</sub>-AcOH to 3-ketopregnan-21-oic acid, m.p. 170—172° (Me ester, m.p. 121—123°), whence it is regenerated by H<sub>2</sub>-PtO<sub>2</sub> in dioxan at 3 atm. Na-EtOH reduces (XI) to pregnane-3( $\beta$ ) : 21-diol, m.p. 164—166° (diacetate, m.p. 76—79°; pregnane-3( $\alpha$ ) : 17-diol, m.p. 205—206°, is similarly prepared. R. S. C.

## V.—TERPENES AND TRITERPENOID SAPOGENINS.

**Reactions of  $\beta$ -pinene. II.** With selenium dioxide in acetic acid W. D. Stallcup and J. E. Hawkins (*J. Amer. Chem. Soc.*, 1942, **64**, 1807—1809; cf. A., 1942, II, 178).— $\beta$ -Pinene and SeO<sub>2</sub> in Ac<sub>2</sub>O (less good, AcOH) give pinocarvyl acetate (I) with some carvopinone (II), pinocarvone (III), and, in AcOH, pinocarveol (IV); the amount of SeO<sub>2</sub> used is of minor importance. SeO<sub>2</sub> in boiling EtOH converts (IV) mainly into (II). Hydrogenation (Pd-C; cyclohexane; 100°/1200 lb.) of (IV) gives *d*-cis-pinocampeol, m.p. 55.5—56°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +39° in Et<sub>2</sub>O, of (I) gives *d*-cis-pinocamphyl acetate, b.p. 80—82°/2—3 mm., 227—228° (corr.)/760 mm., [ $\alpha$ ]<sub>D</sub><sup>25</sup> +23°, of (II) gives *l*-trans-pinocamphone (V), b.p. 212° (corr.), [ $\alpha$ ]<sub>D</sub><sup>25</sup> -13.5° [semicarbazone, m.p. 227.5—228° (corr.)], and of (III) gives a pinocamphone, b.p. 75°/2—3 mm.,  $\alpha_D$  -29° ( $\beta$ -semicarbazone, m.p. 185°). The method of formation and structure of the ketones are discussed. R. S. C.

**Preparation and properties of camphormonoamides.** M. Delépine (*Ann. Chim.*, 1942, [xi], **17**, 171—178).—*d*- $\alpha$ - (combines with EtOH, COMe<sub>2</sub>, but not with H<sub>2</sub>O) and *d*- $\beta$ -camphoramides have vals. of

[ $\alpha$ ]<sub>D</sub> of +25° and +73.2°, respectively, in EtOH. *iso*Camphoric acid and SOCl<sub>2</sub> at room temp., followed by NH<sub>3</sub>-Et<sub>2</sub>O, give *l*- $\alpha$ -*isocamphoramide*, m.p. 193°, [ $\alpha$ ]<sub>D</sub> -46.4° in EtOH, *l*-*isocamphordi*-amide monohydrate, m.p. 132°, [ $\alpha$ ]<sub>D</sub> -37.8° in H<sub>2</sub>O (anhyd., [ $\alpha$ ]<sub>D</sub> -41.25° in H<sub>2</sub>O), and a neutral substance, C<sub>10</sub>H<sub>16</sub>ON<sub>2</sub>, m.p. 187°, [ $\alpha$ ]<sub>D</sub> -82.8° in EtOH. *l*- $\beta$ -*isocamphoramide* (modified prep.), new m.p. 171° (block), has [ $\alpha$ ]<sub>D</sub> -51.4° in EtOH. *l*-*isocamphoric* acid is converted into the *l*- $\alpha$ -Et ester, and thence by SOCl<sub>2</sub> into its  $\beta$ -acid chloride, which with NH<sub>3</sub>-Et<sub>2</sub>O, followed by aq. NH<sub>4</sub>Cl, yields *Et* *a*-*isocamphorate*  $\beta$ -amide, m.p. 121°, [ $\alpha$ ]<sub>D</sub> -51.5° in EtOH (corresponding Me ester, [ $\alpha$ ]<sub>D</sub> -63.2° in EtOH). *d*-Camphoric acid and SOCl<sub>2</sub>, followed by NH<sub>3</sub>-Et<sub>2</sub>O, yield (mainly) camphoric anhydride and *d*- $\alpha$ -camphoramide acid. *d*- $\alpha$ -, m.p. 248° (block), [ $\alpha$ ]<sub>D</sub> +37.3° in EtOH, and *d*- $\beta$ -camphormethylamide, m.p. 178° (block), [ $\alpha$ ]<sub>D</sub> +65.9° in EtOH, are prepared. A. T. P.

**Hydrolysis of amides.** M. Delépine and M. Badoche (*Compt. rend.*, 1942, **214**, 588, 591, and *Ann. Chim.*, 1942, [xi], **17**, 183—212).—*d*-CHPhEt·CO·NH<sub>2</sub>, m.p. 81°, [ $\alpha$ ]<sub>D</sub> +52.6° in EtOH, and 2N-HCl at 100° (bath) give the *d*-acid, whereas boiling 2N-NaOH affords almost entirely the *r*-acid owing to racemisation of the amide prior to hydrolysis. Although *d*-CHPhEt·CO·NHPh, m.p. 81.5°, [ $\alpha$ ]<sub>D</sub> +102° in EtOH, is stable to boiling 2N-HCl, boiling 2N-NaOH (4 hr.) causes partial racemisation; EtOH-NaOH (21 hr.), gives inactive acid + anilide. *r*-NH<sub>2</sub>·CHPh·CH(OH)·CO·NH<sub>2</sub> and aq. Ba(OH)<sub>2</sub> yield two *r*-acids, m.p. 240° (block) and 290° (block) (10%), but 2N-HCl causes little isomerisation, giving mainly the former. *d*- $\alpha$ -Camphoramide (I) and boiling H<sub>2</sub>O give *d*-camphoric acid (II), [ $\alpha$ ]<sub>D</sub> +48.8° in EtOH, and camphoric anhydride (62.5% conversion); the  $\beta$ -amide (III) similarly gives some anhydride and probably some  $\alpha$ -amide. Camphoric acid and boiling H<sub>2</sub>O yield no anhydride; the latter reacts slowly with boiling H<sub>2</sub>O. A mixture of (NH<sub>4</sub>)<sub>2</sub> camphorate, anhydride, and H<sub>2</sub>O in a sealed tube at 100° affords some  $\alpha$ -amide. (I) and boiling 2N-HCl give (II) and 10% of camphorimide (IV); 61% of (II) and 39% of (IV) are obtained similarly from (III), and (III)-20% HCl give 50—70% of (IV). (I) is slowly hydrolysed by 5N-NaOH (8 hr.) to give camphoric acid containing 20% of *l*-iso-acid (V), separable by AcCl at room temp.; similarly after boiling (III) for 15 hr., 50% of (III), 25% of (II), and 3.5% of *iso*-acid, probably formed through (IV) (which can be isolated), are obtained. *l*- $\alpha$ - (VI) and  $\beta$ -*isocamphoramide* (VII) are unaltered by boiling H<sub>2</sub>O, but are hydrolysed ( $\alpha$ - more readily) by 2N-HCl to (V); no imide nor anhydride is formed. Alkaline hydrolysis of (VI) gives (V) and some (II). (VII) is difficult to hydrolyse; after boiling with 4N-NaOH for 4 hr., a trace of *d*-acid is formed. *l*-*isocamphordiamide* (VIII) and boiling 2N-HCl (8 hr.) give (V) and (VI), whereas (VIII) and N-NaOH (10 hr.) yield *d*- $\beta$ -*cis*-camphoramide, rotation becoming positive. (V) shows only 1.3% conversion into *d*-acid on boiling with 5N-NaOH for 8.5 hr. *d*- $\alpha$ -Camphormethylamide (IX) reacts slowly with boiling H<sub>2</sub>O, giving probably some *d*- $\beta$ -methylamide (X); (X) similarly yields 21% of anhydride and (IX). (IX) can be isolated from a mixture of camphoric acid neutralised with NH<sub>2</sub>Me, anhydride, and H<sub>2</sub>O, heated in a sealed tube at 100° for 3 hr. (IX) and, more readily, (X) are converted by 2N-HCl into the methylimide, m.p. 42—43°, [ $\alpha$ ]<sub>D</sub> +11.4° in EtOH. *cis*-Hexahydro-*p*-toluamide (XI), refluxed with 2N-HCl for 7 hr., is partly transformed (15%) into the *trans*-amide (XII); (XI) and aq. NaOH-EtOH yield 35% of (XII), and excess of alkali affords 50% of the *trans*-acid (XIII), m.p. 111°. (XII) is not isomerised, and yields only (XIII). In general, acids saponify the amides with liberation of the corresponding acid, whereas alkalis often cause racemisation or isomerisation, probably owing to keto-enol change CR<sub>2</sub>:C(OH)·NH<sub>2</sub>. A. T. P.

**Configuration of nickel bisformylcamphor-ethylenediamine.**—See A., 1943, I, 5.

**Reactivity of terpene nuclei. Halogenation of dihydroterpenes.** A. Gandini (*Gazzetta*, 1941, **71**, 722—729).—A review (cf. Gandini, A., 1936, 1257; 1939, II, 220; 1940, II, 283; *Gazzetta*, 1940, **70**, 604). In the halogenation of dihydroterpenes, Me and Pr <sup>$\beta$</sup>  groups are unaffected, the nucleus being attacked. In dicyclic terpenes, halogenation is first in the  $\beta$ -position to C<sub>(7)</sub>, in contrast to menthane, first halogenated at C<sub>(4)</sub>. E. W. W.

## VI.—HETEROCYCLIC.

**Reaction of furoic acid with aromatic compounds.**—See A., 1943, II, 34.

**Alkylquinols and related compounds.**—See A., 1943, II, 29.

**Nitration of 5-hydroxy-4-methylcoumarin and 5-hydroxy-4-methylcoumarin-6-carboxylic acid and its methyl ester.** N. B. Parekh and R. C. Shah (*J. Indian Chem. Soc.*, 1942, **19**, 335—338).—5-Hydroxy-4-methylcoumarin with HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> at 0° gives the 8-NO<sub>2</sub>-derivative (I), m.p. 174—176° (efferv.), and at room temp., the 6 : 8-(NO<sub>2</sub>)<sub>2</sub>-compound, m.p. 181—182°. Me 5-hydroxy-4-methylcoumarin-6-carboxylate with AcOH-HNO<sub>3</sub> affords the 8-NO<sub>2</sub>-derivative, m.p. 201—202°, hydrolysed to the corresponding acid, m.p. 220—221°, also obtained by nitration of 5-hydroxy-4-methyl-

coumarin-6-carboxylic acid, and decarboxylated (AcOH-HCl) to (I). F. R. S.

**Aluminium chloride**—reagent for the condensation of  $\beta$ -ketonic esters with phenols. **VII. Condensation of 4-nitroresorcinol with ethyl acetoacetate.** N. B. Parekh and R. C. Shah (*J. Indian Chem. Soc.*, 1942, **19**, 339—342).—4 : 1 : 3-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(OH)<sub>2</sub> and CH<sub>3</sub>Ac·CO<sub>2</sub>Et in PhNO<sub>2</sub> with AlCl<sub>3</sub> give, in poor yield, 6-nitro-5-hydroxy-4-methylcoumarin (I), m.p. 209—210° (Me ester, m.p. 132—133°), which is converted by Me<sub>2</sub>SO<sub>4</sub>-NaOH successively into 5-nitro-6-hydroxy-2-methoxy- (+0.5H<sub>2</sub>O), m.p. 162—163° (efferv.), and 5-nitro-2 : 6-dimethoxy- $\beta$ -methylcinnamic acid, m.p. 206—208°. The formation of (I) in the condensation indicates chelation between NO<sub>2</sub> and OH in the resorcinol. F. R. S.

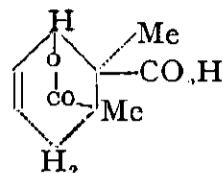
**Dibenzfurans.**—See B., 1943, II, 6.

**Synthesis of cantharidin.** K. Ziegler, G. Schenck, and E. W. Krockow [with A. Siebert, A. Wenz, and H. Weber] (*Annalen*, 1942, **551**, 1—79).—Me<sub>2</sub> 3 : 6-endomethylenehexahydrophthalate is converted by CPh<sub>3</sub>Na at room temp. followed by MeI (better Me<sub>2</sub>SO<sub>4</sub>) and hydrolysis into *cis*-1 : 2-dimethyl-3 : 6-endomethylenehexahydrophthalic anhydride ("methylenecantharidin"), m.p. 206° (Me<sub>2</sub> ester of the corresponding acid, m.p. 57°), with a small proportion of *trans*-1 : 2-dimethyl-3 : 6-endomethylenehexahydrophthalic acid, m.p. 320—323° (Me<sub>2</sub> ester, m.p. 44°); the *exo*-anhydride does not appear to be formed. Attempts to methylate Me<sub>2</sub> norcantharidate similarly were unsuccessful.

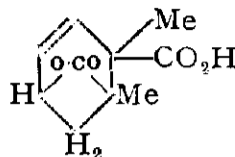
*trans*- $\Delta^4$ -Tetrahydrophthalodinitrile, m.p. 125°, is obtained in small yield from fumaronitrile (prep. from the diamide, *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>Cl, and anhyd. C<sub>5</sub>H<sub>5</sub>N described), (CH<sub>2</sub>:CH)<sub>2</sub>, and PhMe at 100° but the change is accompanied by the formation of much rubber-like polymeride. This is avoided by passing the gas into the dinitrile and PhMe at 170—180°, when a 76% yield is very slowly obtained. It does not appear to be methylated smoothly. 1 : 2-Dimethyl- $\Delta^4$ -tetrahydrophthalic anhydride (I), m.p. 101°, is obtained with much polymeride when (CMe·CO)<sub>2</sub>O and (CH<sub>2</sub>:CH)<sub>2</sub> are heated in a sealed tube; the yield attains 50% when the gas is passed into a solution of the anhydride in decahydronaphthalene at 192° in 720 hr. and 60% when the reactants without solvent are heated at 170—180° in an autoclave of such size that the bulk of the (CH<sub>2</sub>:CH)<sub>2</sub> remains in the gaseous phase. (I) is stable at 400° and is hydrolysed by alkali to the acid, m.p. 200° with re-formation of (I), which also slowly results when a solution of the acid in H<sub>2</sub>O is boiled. It is hydrogenated to 1 : 2-dimethylhexahydrophthalic anhydride (II), m.p. 129°, identical with the deoxycantharidin of Gadamer (A., 1917, i, 659, 704); the corresponding acid, m.p. 180°, passes partly into the anhydride in boiling H<sub>2</sub>O. The characteristic instability of the cantharidindicarboxylic acids is therefore due to the presence of the bridge. (I) and Br in CCl<sub>4</sub> (small quantities should be used or, better in AcOH) afford 4 : 5-dibromo-1 : 2-dimethylhexahydrophthalic anhydride, m.p. 181°, which is rapidly converted by boiling aq. NaOH into an anhydride, C<sub>10</sub>H<sub>12</sub>O<sub>4</sub>, m.p. 182° (vac.), and the corresponding dicarboxylic acid, C<sub>10</sub>H<sub>14</sub>O<sub>5</sub>, m.p. 178°. Other reagents for the elimination of HBr give uninviting products but NMe<sub>3</sub> at 100° gives large amounts of non-volatile products and ~10% of 1 : 2-dimethyl-1 : 2-dihydrophthalic anhydride (III), b.p. 112°/2 mm., m.p. 70°. (III) is quantitatively hydrogenated to (II), is converted by alkali and cold acid into the corresponding acid, m.p. 158° with re-formation of (III), and with Br in AcOH yields at least two dibromides, the most sparingly sol. of which has m.p. 126°. This loses only 1 Br when treated with different reagents, e.g., AgNO<sub>3</sub> in EtOH or aq. COMe<sub>2</sub>. (III) and NH<sub>3</sub> at 250° yield 1 : 2-dimethyl-1 : 2-dihydrophthalimide, m.p. 136°, the dehydrocantharidinimide of Gadamer (*loc. cit.*). (I) and (CH<sub>2</sub>:CO)<sub>2</sub>NBr in boiling CCl<sub>4</sub> give a mixture (IV) of 6-bromo-1 : 2-dimethyl- $\Delta^4$ -tetrahydrophthalic anhydrides, separated by crystallisation into a small proportion of a stable monobromide, m.p. 106°, and a large proportion of an isomeride, m.p. 72°, which tends to lose HBr spontaneously. When heated at 150° and then at 180° (IV) gives (III) in variable yield dependent on experimental conditions. Boiling 20% NaOH hydrolyses (IV) to isocantharic acid B (V), m.p. 204—206° [Me ester (VI), m.p. 72°], converted by boiling AcCl into 6-acetoxy-1 : 2-dimethyl- $\Delta^4$ -tetrahydrophthalic anhydride, b.p. 310°, m.p. 101.5—102°, identical with the substance obtained by oxidising (I) with SeO<sub>2</sub>-Ac<sub>2</sub>O. (V) is reduced (Pd-BaSO<sub>4</sub> in abs. EtOH) to dihydrocantharic acid, m.p. 263° [Me<sub>2</sub> ester (VII), m.p. 58—60°]. (VI) and (CH<sub>2</sub>:CO)<sub>2</sub>NBr at 130—135° afford Me bromoisocantharate, m.p. 166°, converted by H<sub>2</sub>-Pd-BaSO<sub>4</sub> into (VII), m.p. 65°. Treatment of the non-volatile products of the prep. of (III) with boiling aq. NaOH followed by acid gives  $\psi$ -cantharic acid (VIII), m.p. 187° (Me ester, m.p. 100°; H<sub>2</sub>-derivative, m.p. 270—273°).

(CMe·CO)<sub>2</sub>O and cyclohexadiene, best in presence of C<sub>6</sub>H<sub>6</sub>, at 170—180° afford 1 : 2-dimethyl-3 : 6-endovinylenehexahydrophthalic anhydride (IX), m.p. 263.5°, oxidised by NaOBr to the bromolactonic acid, C<sub>12</sub>H<sub>15</sub>O<sub>4</sub>Br, m.p. 231—232° (discoloration, decomp.) (Me ester, m.p. 164—165°), and further to the mutually interconvertible dilactone, C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>, m.p. ~375°, or hydroxylactonic acid, C<sub>12</sub>H<sub>16</sub>O<sub>5</sub>·H<sub>2</sub>O, m.p. ~375° (Me ester, m.p. 177—178°). (IX) is converted by dissolution in NaOH and oxidation with KMnO<sub>4</sub> into

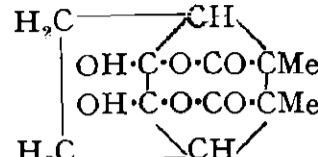
1 : 2-dimethyl-3 : 6-endodihydroxyethylenehexahydrophthalic anhydride [3 : 6-endodihydroxyethylenedioxycantharidin] (X), m.p. 303°, transformed by COMe<sub>2</sub> containing a few drops of conc. H<sub>2</sub>SO<sub>4</sub> into the CMe<sub>2</sub> ether, m.p. 214—215°. (X) is converted by HNO<sub>3</sub> (d 1.5) at 100° into the dinitrate, m.p. 157—158°. HNO<sub>3</sub> (d 1.2) oxidises (X) at 100° to 4 : 5-diketo-1 : 2-dimethyl-3 : 6-endoethylenehexahydrophthalic acid (+H<sub>2</sub>O); the colourless form is probably (A). It becomes yellow at >260° (diketon form) and has m.p. 315—320° when slowly heated, 338—340° (decomp.) in bath preheated to 330°.



(V.)



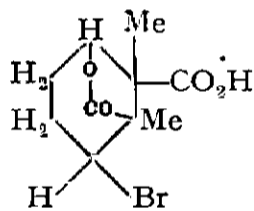
(VIII.)



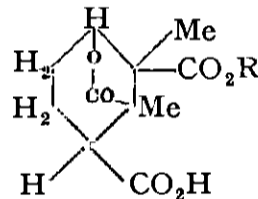
(A.)

It is converted by CH<sub>2</sub>N<sub>2</sub> into the yellow Me<sub>2</sub> ester, m.p. 173—174°, and by boiling Ac<sub>2</sub>O into the yellow anhydride (m.p. as for acid), which spontaneously absorbs H<sub>2</sub>O and becomes colourless when exposed to air. The acid is transformed by evaporation with fuming HNO<sub>3</sub> into *cis*-1 : 2-dimethylcyclohexane-1 : 2 : 3 : 6-tetracarboxylic dianhydride (XI), m.p. 245—246°, converted by boiling H<sub>2</sub>O into the tetracarboxylic acid. (XI) is transformed by prolonged action of CH<sub>2</sub>N<sub>2</sub> in aq. Et<sub>2</sub>O into the corresponding *cis*-Me<sub>2</sub> ester (XII), m.p. 108—109°, whereas in aq. COMe<sub>2</sub> a *cis*-Me<sub>2</sub> ester, m.p. 156°, results, converted by further methylation (CH<sub>2</sub>N<sub>2</sub>) into (XII). Neutralisation (phenolphthalein) of (XI) with NaOMe-MeOH, addition of HCl (Congo-red), and treatment of the product with CH<sub>2</sub>N<sub>2</sub> leads to (XII), whereas evaporation of the solution to dryness and treatment of the residue with Me<sub>2</sub>SO<sub>4</sub>-NaOMe under strictly defined conditions gives Me<sub>4</sub> 1 : 2-dimethylcyclohexane-*cis*-1 : 2-*trans*-3 : 6-tetracarboxylate (XIII), m.p. 111—112°. This is partly hydrolysed by alkali to the 1 : 2-Me<sub>2</sub> 3 : 6-H<sub>2</sub> ester (+H<sub>2</sub>O) (lost at 120°), m.p. 208°, also obtained by acid hydrolysis (20.2% HCl) of (XIII). 20.2% HCl and (XII) yield essentially the 1 : 2-Me<sub>2</sub> 3 : 6-H<sub>2</sub> ester.

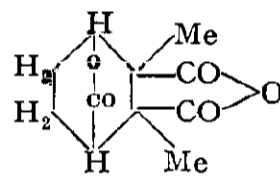
(XIII) is neutralised with 2N-NaOH and transformed under strictly defined conditions into the Ag<sub>2</sub> salt, which is converted by Br in CCl<sub>4</sub> into acidic products (XIV) and a "neutral oil" from which Me epihydrobromocantharate, m.p. 115—116°, is isolated. It is hydrolysed by boiling 48% HBr to the acid (XV), anhyd. or +1H<sub>2</sub>O, m.p. 185—186°, which, when heated, affords cantharic acid and



(XV.)



(XVI.)



(XVII.)

cantharidin. (XIV) contain 4-bromo-2 : 3-dicarbomethoxy-2 : 3-dimethylcyclohexane-1-carboxylic acid, m.p. 119°, and the ester lactone (XVI) (R = Me), m.p. 184—185°, hydrolysed by 48% HBr to the lactonedicarboxylic acid (XVI) (R = H), m.p. 296—297° (change at 205—220°), also obtained as a by-product of the prep. of (XV); it is transformed by boiling Ac<sub>2</sub>O into the anhydride (XVII), m.p. 296—297°. The configuration of cantharidin is discussed. H. W.

**Cleavage of ethylene linkage by thionyl chloride.** A. Schönberg and W. Asker (*J.C.S.*, 1942, 725).—Dixanthylene (I), dithioxanthylene, NN'-dimethyldiacridine, diflavylene, and dithioflavylene undergo cleavage when boiled with SOCl<sub>2</sub> and the product dissolved in C<sub>6</sub>H<sub>6</sub> and shaken with H<sub>2</sub>O at 30°, yielding the ketones. The product from (I) and SOCl<sub>2</sub> with NH<sub>2</sub>Ph yields xanthoneanil.

A. Li.

**Synthesis of a 3 : 4-diaminotetrahydrothiophen and a comparison of its stability with the diaminocarboxylic acid derived from biotin.** G. W. Kilmer, M. D. Armstrong, G. B. Brown, and V. du Vigneaud (*J. Biol. Chem.*, 1942, **145**, 495—501; cf. A., 1942, II, 387).—dl-[CH<sub>2</sub>Br·CH(OH)]<sub>2</sub> and aq. Na<sub>2</sub>S at 50—60°, then at 100°, followed by treatment of the product with HCl in a sealed tube at 150° or with HBr (reflux) give 3 : 4-dichloro-, m.p. 60—61°, or -dibromotetrahydrothiophen, m.p. 83—89°; attempted replacement of halogen by the use of NH<sub>3</sub>, o-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NK, and other reagents was unsuccessful, as also were attempts to replace Br in the derived sulphone.  $\alpha\delta$ -Dichlorobutane- $\beta$ -*γ*-diol, m.p. 62—63°, b.p. 113—118°/4 mm., obtained by KMnO<sub>4</sub> oxidation of  $\alpha\delta$ -dibromo- $\Delta^2$ -butene, is converted by aq. Na<sub>2</sub>S into 3 : 4-dihydroxytetrahydrothiophen, m.p. 54—58° (HI at 210° gives much H<sub>2</sub>S). Et<sub>4</sub> tetrahydrothiophen-3 : 3 : 4 : 4-tetracarboxylate (I) (modified prep.), b.p. 200—208°/8 mm., and n-NaOH at 80°, followed by heating the residue at 140—160°, esterification to the di-ester with HCl-EtOH at room temp., and heating with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (water-bath), afford tetrahydrothiophen-3 : 4-dicarboxylic dihydrazide (II), m.p. 226—227° (previous softening), also obtained in lower yield by partial hydrolysis of (I) with 0.1N-NaOH at room temp., followed by decarboxylation and treatment with N<sub>2</sub>H<sub>4</sub>. (II) and NaNO<sub>2</sub> in n-HCl-Et<sub>2</sub>O followed by interaction of the azide with EtOH give 3 : 4-diurethanotetrahydrothiophen,

m.p. 176—178°, converted by HCl (sealed tube; 100—105°) into 3,4-diaminotetrahydrothiophen dihydrochloride, incipient decomp. ~250° [aq. NaOH gives the free diamine (III), m.p. ~40°; dipicrate, incipient decomp. ~250°;  $Ac_2$ , sublimes at 260—265°, and  $Bz_2$  derivative, m.p. 295—300° (previous softening)]. A cyclic urea derivative could not be obtained by treating (III) with  $COCl_2$ -NaOH, and  $Et_2CO_3$  did not yield a CO<sub>2</sub> derivative. (III) is unchanged with fuming HI at 210°, but at 250° ~5—10% of its S is liberated as H<sub>2</sub>S, and 10—15% of its N as volatile base; it is thus more stable than the diaminocarboxylic acid derived from biotin. A. T. P.

**1-p-Aminobenzenesulphonamido-2:5-dimethylpyrrole.** E. O'F. Walsh (J.C.S., 1942, 726).—p-Acetamidobenzenesulphonhydrazide and acetonylacetone in AcOH give 1-p-aminobenzenesulphonamido-2:5-dimethylpyrrole, m.p. 202° (decomp.), after hydrolysis (NaOH). 1-p-Toluenesulphonamido-2:5-dimethylpyrrole, m.p. 144°, is similarly prepared. F. R. S.

**Synthesis of vitamin B<sub>6</sub>.**—See B., 1943, III, 21.

**Some anilinopyridine derivatives.** W. O. Kermack and (Miss) A. P. Weatherhead (J.C.S., 1942, 726).—From the appropriate Cl-derivative and NH<sub>2</sub>-compound, the following have been prepared: 2-anilino-, m.p. 263°, and 2-p-anisidinonicotinic acid, m.p. 295°, 4-anilinopyridine, m.p. 173°, N-(4'-pyridyl)anthranilic acid hydrochloride, m.p. 185°, and N-(3'-pyridyl)anthranilic acid, m.p. 238°. These acids could not be cyclised with either H<sub>2</sub>SO<sub>4</sub> or POCl<sub>3</sub>. F. R. S.

**Préparation of certain 3-substituted indoles.** (Mrs.) R. H. Cornforth and (Sir) R. Robinson (J.C.S., 1942, 680—682).—Indole and indole-2-carboxylic acid (I) are converted by MeOH-NaOMe at 210—220° into skatole, which may be conveniently prepared in this way. Treatment of (I) with the appropriate alcohol gives the following: 3-ethyl- (picrate, m.p. 121°), 3-n-propyl-, b.p. 162—164°/20 mm., 3-n-butyl- (picrate, m.p. 114°), 3-n-heptyl-, m.p. 60°, 3-benzyl-, m.p. 103°, 3-γ-phenylpropyl-, m.p. 73°, 3:7-dimethyl-, m.p. 56°, and 3-cyclohexyl-7-methyl-indole, m.p. 115°. (I) could not be alkylated by means of sec. alcohols and their Na derivatives. A mechanism for the reaction is suggested. F. R. S.

**Reaction with hydrazoic acid in sulphuric acid. IV. Behaviour of substances containing the system -CO-CO-NH-.** G. Caronna (Gazzetta, 1941, 71, 585—589).—Isatin (or acetylisatin) with NaN<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> gives anthranilamide; N-ethylisatin gives o-ethylaminobenzamide. CPh·CO·NHPh gives the same products as benzil (cf. Spielman *et al.*, A., 1938, II, 64). E. W. W.

**Synthesis of 4:5-dihydroxyquinoline.** L. Musajo and (Signa.) M. Minchilli (Gazzetta, 1941, 71, 762—765).—3:4:1-NH<sub>2</sub>·C<sub>8</sub>H<sub>3</sub>Cl·OH and CO<sub>2</sub>Me·CH<sub>2</sub>·CO·CO<sub>2</sub>Me in boiling Et<sub>2</sub>O give Me<sub>2</sub> 2-chloro-5-hydroxyanilosuccinate, m.p. 101—102°, which in petroleum jelly at 220° gives Me 8-chloro-4:5-dihydroxyquinoline-2-carboxylate, m.p. 143°, reduced in aq. MeOH-NaOAc by H<sub>2</sub> (Pd-C) to the Me ester, m.p. 253°, of 4:5-dihydroxyquinoline-2-carboxylic acid, m.p. 305° (decomp.). Above its m.p. this yields 4:5-dihydroxyquinoline, m.p. 231—232°. E. W. W.

**Utilisation of alkoxy-ketones in the synthesis of quinolines by the Pfitzinger reaction. II.** S. D. Lesesne [with H. R. Henze] (J. Amer. Chem. Soc., 1942, 64, 1897—1900; cf. A., 1939, II, 388; 1940, II, 24).—Isatin and COEt·CHMe·OMe, b.p. 154—155°/746 mm. (semicarbazone [Wallace], m.p. 120·5°), in 33% aq. KOH at 100° give 3-methyl-2-α-methoxyethylcinchonic acid (I) (74%), m.p. 234° (decomp.) [Me ester, m.p. 57° (picrate, m.p. 179°)]. At 250° (I) gives CO<sub>2</sub> and, by fission and reduction, 3-methyl-2-ethylquinoline (14%) [picrate, m.p. 191° (corr.) (lit. 193°)], with conc. HCl at 100° gives 3-methyl-2-α-hydroxyethylcinchonic acid (55%), +H<sub>2</sub>O, m.p. 265° (picrate, explodes at >310°), with boiling HI-red P gives, after 6 hr., 3-methyl-2-ethylcinchonic acid (II) (78%), m.p. 279° (picrate, m.p. 198°), or, after 7 days, 3-methyl-2-ethyl-1:2:3:4-tetrahydroquinoline (III) (70%), b.p. 253°/716 mm. (picrate, m.p. 188°), and with H<sub>2</sub>-PtO<sub>2</sub> in EtOH gives 3-methyl-2-α-methoxyethyl-1:2:3:4-tetrahydrocinchonic acid, m.p. 232° (decomp.). (III) suffers fission by Sn-HCl at 100°, giving 3-methyl-1:2:3:4-tetrahydroquinoline, b.p. 117°/15 mm. [picrate, m.p. 159° (corr.) (lit. 155°)]. With SOCl<sub>2</sub> at 0° and then the appropriate amine, (I) gives 3-methyl-2-α-methoxyethylcinchondi-ethyl- (IV), m.p. 94°, -isoamyl-, m.p. 190°, and -allyl-amide, m.p. 112°, and, by NH[(CH<sub>2</sub>)<sub>2</sub>·OH], the diester-amide, (RCO<sub>2</sub>·[CH<sub>2</sub>)<sub>2</sub>·NH, m.p. 200°. (II) gives similarly 3-methyl-2-ethylcinchondi-ethyl- (V), m.p. 100°, -isoamyl-, m.p. 132°, and -allyl-amide, an oil, and the diester-amide, (RCO<sub>2</sub>·[CH<sub>2</sub>)<sub>2</sub>·NH, m.p. 295°. Isatin and COMe·CHMe·OMe, b.p. 115—116°/739 mm. (semicarbazone [Wallace], m.p. 141°), lead similarly to 2-α-methoxyethylcinchonic acid, m.p. 186° (decomp.), 2-ethylcinchonic acid, m.p. 180°, and 2-ethylquinoline [picrate, m.p. 148° (lit. 147°)]. With isatin in KOH, acetoin and CPhPr<sup>a</sup> give bis-2-cinchonic acid [di-4-carboxy-2-quinolyl] (VI) (58%), m.p. 367° [diethylamide (VII), m.p. 257°], and 2-phenyl-3-ethylcinchonic acid (VIII), m.p. 286° [picrate, m.p. 147°; diethylamide (IX), m.p. 244°], respectively. M.p. are corr. Inactivity is recorded as follows: (I), (II), (VI), (VIII), and (IX)

against *Plasmodium cathemerium* in canaries; (IV), (V), and (VIII) against avian malaria; (VII) orally against *Streptococcus viridans* in mice. R. S. C.

**Acylation experiments with sulphanilamide and heterocyclic amines.**—See A., 1943, II, 28.

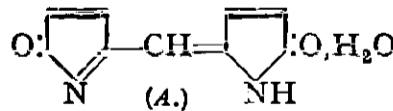
**Quinolines and acridines.**—See B., 1943, II, 6.

**α-Alkoxyvinyl- and α-alkoxyethyl-barbituric acids.** S. M. McElvain and H. Burkett (J. Amer. Chem. Soc., 1942, 64, 1831—1836).—CH<sub>2</sub>:C(OR)<sub>2</sub>, CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>, and NaOR at 125—130° give a mixture, separated for R = Et, of OR·CMe:C(CO<sub>2</sub>Et)<sub>2</sub> (A) and CH<sub>2</sub>:C(OR)·CH(CO<sub>2</sub>Et)<sub>2</sub> (B), which with AlkBr or AlkI in, best (usually 55—85% yield), Pr<sup>β</sup>OH gives CH<sub>2</sub>:C(OR)·CR'(CO<sub>2</sub>Et)<sub>2</sub>, converted by CO(NH<sub>2</sub>)<sub>2</sub> and NaOPr<sup>β</sup>-Pr<sup>β</sup>OH in poor yield into 5-alkyl-5-α-alkoxyvinylbarbituric acids or by H<sub>2</sub>-Raney Ni in EtOH at 120°/1850 lb. into OR·CHMe·CR'(CO<sub>2</sub>Et)<sub>2</sub>, which in EtOH give good yields of 5-alkyl-5-α-alkoxyethylbarbituric acids. Alkylation of OR·CHMe·CH(CO<sub>2</sub>Et)<sub>2</sub> is impossible. The pharmacological properties, sometimes pronounced, are briefly discussed. The following are obtained: Et<sub>2</sub> α-ethoxyethylidene- (I) (66%), m.p. 26—27°, b.p. 79—83°/0·03 mm. (with O<sub>3</sub> gives no CH<sub>2</sub>O), and α-ethoxyvinyl-malonate (II) (11%), b.p. 69—70°/0·03 mm. [with O<sub>3</sub> in AcOH-Ac<sub>2</sub>O gives CH<sub>2</sub>O; with NaOEt at 125° slowly gives (I)]; mixtures of (A) and (B), in which R = Pr, b.p. 110—112°/3 mm., Bu<sup>a</sup>, b.p. 135—140°/2·5 mm., and isoamyl, b.p. 120—130°/0·05 mm.; Et<sub>2</sub> ethyl-α-ethoxy-, b.p. 87—91°/0·1 mm. [prep. from (I) or (II); also obtained from CEFNa(CO<sub>2</sub>Et)<sub>2</sub> by CHMeCl·OEt in C<sub>6</sub>H<sub>6</sub>], -n-propoxy-, b.p. 121—130°/2·3 mm., -n-butoxy-, b.p. 110—120°/0·5 mm., and -isoamyl-, b.p. 104—110°/0·04 mm., -vinylmalonate; Et<sub>2</sub> allyl-, b.p. 92—96°/0·1 mm., -n-propyl-, b.p. 97—98°/1 mm., -n-butyl-, b.p. 88—91°/0·04 mm., and isoamyl-, b.p. 84—90°/0·01 mm., -α-ethoxyvinylmalonate; Et<sub>2</sub> ethyl-α-ethoxy-, b.p. 71—72°/0·03 mm., -n-propoxy-, b.p. 77—78°/0·03 mm., -n-butoxy-, b.p. 83—84°/0·03 mm., -isoamyl-, b.p. 89—90°/0·03 mm., -ethylmalonate; Et<sub>2</sub> α-ethoxyethyl-n-propyl-, b.p. 81—82°/0·03 mm., -n-butyl-, b.p. 85—86°/0·04 mm., -isoamyl-, b.p. 88—89°/0·03 mm., -allyl-, b.p. 78—79°/0·04 mm., and -sec.-amyl-, b.p. 83—84°/0·03 mm., -malonate; Et<sub>2</sub> α-propoxyethyl-allyl-, b.p. 97—98°/0·18 mm., and -sec.-amyl-malonate, b.p. 101—102°/0·06 mm.; 5-ethyl-5-α-ethoxy-, m.p. 189·5—190°, -n-propoxy-, m.p. 177—179°, and -isoamyl-, m.p. 153—154°, -vinylbarbituric acid; 5-α-ethoxyvinyl-5-allylbarbituric acid, m.p. 158—160°; 5-n-butyl-, m.p. 169—170°, and 5-isoamyl-5-α-ethoxyvinylbarbituric acid, m.p. 165·5—166°; 5-ethyl-5-α-ethoxy-, m.p. 181—181·5°, -n-propoxy-, m.p. 177·5—178°, -n-butoxy-, m.p. 132·5—133°, and -isoamyl-, m.p. 129·2—130°, -ethylbarbituric acid; 5-α-ethoxyethyl-5-n-propyl-, m.p. 168·5—169°, -n-butyl-, m.p. 138—139°, -isoamyl-, m.p. 136—137°, -allyl-, m.p. 127—128°, and -sec.-amyl-, m.p. 169—169·5°, -barbituric acid; 5-α-n-propoxyethyl-5-allyl-, m.p. 160—160·5°, and -sec.-amyl-barbituric acid, forms, m.p. 210·5—212° and 153·5—154·5°. R. S. C.

**2-Sulphanilamidopyrimidine.**—See B., 1942, III, 21.

**Pentduopent reaction. V.** H. von Döbeneck (Z. physiol. Chem., 1942, 275, 1—15).—Prep. of propentduopent (A) solutions, essentially by alkaline H<sub>2</sub>O<sub>2</sub>, from hæmin, bilirubin (I), biliverdin, urobilin, stercobilin, and blood is described and absorption max. of the products are recorded. Animal organs, urine, pneumococci, and icterus serum do not give the pentduopent (B) reaction, i.e., a red colour on treatment of solutions of (A) with alkaline Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. A positive reaction by urine indicates presence of hæmin. (A) are considered to include the structure shown and (B) to be 5:5'-dihydroxypyrrmethenes (or the derived CO-form). This is supported by analysis of the propentduopent from (I), the Zn salt of that from the Me<sub>2</sub> ester of opsin acid-methene, the Cu salt of that from ætiohæmin-I, and the Me<sub>2</sub> ester of 5:5'-dihydroxy-3:3'-dimethylpyrrmethene-4:4'-dipropionic acid, and by the following results. Et 3-formyl-2:4-dimethyl- with H<sub>2</sub>-Raney Ni in EtOH at 160°/150 atm. gives Et 2:3:4-trimethylpyrrole-5-carboxylate (60%), m.p. 127° (and, sometimes, a dimeride, m.p. 228°, of Et 2:4-dimethylpyrrole-5-carboxylate). 2:2'-Dibromo-3:4:3':4'-tetramethylpyrrmethene with boiling KOAc-AcOH-H<sub>2</sub>O gives 5:5'-dihydroxy-3:4:3':4'-tetramethylpyrrmethene (>5%), m.p. 211°, which with H<sub>2</sub>O<sub>2</sub>-NaOH gives the 3:4:3':4'-Me<sub>4</sub> derivative, m.p. 223°, of (A) and with H<sub>2</sub>-PtO<sub>2</sub> in MeOH gives the derived pyrromethane, m.p. 214°. 5:5'-Dihydroxy-4:4'-dicarbomethoxy-3:3'-dimethylpyrrmethane, m.p. 147°, is obtained from the corresponding (A) or (B). R. S. C.

**Bile pigments. XXXV. Synthesis of biliverdin (uteroverdin), bilirubin, biliverdins XH<sub>1</sub>α and IIIα, and of vinylneoxanthic acid.** H. Fischer and H. Plieninger (Z. physiol. Chem., 1942, 274, 231—260).—Opsopyrrolecarboxylic acid is converted by H<sub>2</sub>O<sub>2</sub> in C<sub>5</sub>H<sub>5</sub>N at 55° into β-5- (I), m.p. 183°, with a smaller amount of -2- (II), m.p. 140—145°, -hydroxy-4-methylpyrrole-3-propionic acid. (I) is converted (MeOH-HCl, not CH<sub>3</sub>N<sub>2</sub>) into the Me ester, m.p. 85—87°, and thence by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in boiling MeOH into the hydrazide,



m.p. 148°. This is converted by  $\text{HNO}_2$  at  $-5^\circ$  into the unstable azide, transformed by boiling  $\text{EtOH}$  into 5-hydroxy-4-methyl-3-carbethoxyaminoethylpyrrole (III), m.p. 80–85°, which could not be hydrolysed to the amine by acid or alkali by reason of the instability of the pyrrole ring. (III) is condensed with opsopyrrolealdehyde (IV) in alkaline medium to 5-hydroxy-4:3'-dimethyl-3- $\beta$ -carbethoxyaminoethylpyrromethene-4-propionic acid (V), m.p. 205°, which with  $\text{CH}_2\text{O}-\text{HCl}$  affords  $\text{Me}_2$  1':8'-dihydroxy-1:3:6:8-tetramethyl-2:7- $\beta$ -carbethoxyaminoethyl-2a:7'-bilidiene-4:5-dipropionate, m.p. 250°. This is dehydrogenated by  $p\text{-O:C}_6\text{H}_4\text{:O}$  in  $\text{AcOH}$  at  $100^\circ$  to the glaucobilinurethane, m.p. 248°, also obtained from (V),  $\text{Ac}_2\text{O}$ , and  $\text{HCO}_2\text{H}$  at  $100^\circ$  and hydrolysed by 18%  $\text{HCl}$  at  $135\text{--}140^\circ$  to 1':8'-dihydroxy-1:3:6:8-tetramethyl-2:7- $\beta$ -aminoethyl-2a:7'-bilidiene-4:5-dipropionic acid dihydrochloride (VI), which when benzoated and esterified ( $\text{MeOH}-\text{HCl}$ ) gives an unidentified compound,  $\text{C}_{49}\text{H}_{52}\text{O}_8\text{N}_6$ , m.p. 145°. Prolongation of the reaction between (III) and (IV) (see above) leads to the unstable 5'-hydroxy-3:4'-dimethyl-3'- $\beta$ -aminoethylpyrromethene-4-propionic acid, m.p. 230–240° [Me ester (VII), m.p. (indef.), 90–120° (decomp.)], benzoated and esterified ( $\text{MeOH}-\text{HCl}$ ) to Me 5'-hydroxy-3:4'-dimethyl-3'- $\beta$ -benzamidoethylpyrromethene-4-propionate, m.p. 235°, which condenses with  $\text{Ac}_2\text{O}-\text{HCO}_2\text{H}$  to  $\text{Me}_2$  1':8'-dihydroxy-1:3:6:8-tetramethyl-2:7-di- $\beta$ -benzamidoethylbilidriene-4:5-dipropionate, m.p. 195–220°. The corresponding -2:7-di- $\beta$ -acetamidoethyl acid (Me<sub>2</sub> ester, m.p. 220°) is hydrolysed by boiling 18%  $\text{HCl}$  to (VI). Methylation ( $\text{NaOH}-\text{Me}_2\text{SO}_4$ ) of (VI) followed by elimination of  $\text{NMe}_3$  and esterification ( $\text{MeOH}-\text{HCl}$ ) leads to biliverdin XIIIa Me<sub>2</sub> ester, m.p. 245° (Kofler), also obtained by the action of  $\text{KOH}-\text{MeOH}$  containing  $\text{Zn}(\text{OAc})_2$  and  $\text{MeI}$  on (VI) and converted by fusion with  $m\text{-C}_6\text{H}_4(\text{OH})_2$  into Me vinylneoxanthobilirubate, m.p. 187°, also obtained from (VII). (II) and 5-formyl-3-acetyl-2:4-dimethylpyrrole after esterification yield Me 5-hydroxy-4'-acetyl-3:3':5'-trimethylpyrromethene-3-propionate, m.p. 250°. (II) is transformed by  $\text{HCl}-\text{MeOH}$  into the Me ester, m.p. (indef.) 45°, and thence successively into the hydrazide, m.p. 162°, azide, and carbethoxyamino-derivative and 5'-hydroxy-3:3'-dimethyl-4'- $\beta$ -carbethoxyaminoethylpyrromethene-4-propionic acid (Me ester, m.p. 227°); this is converted by  $\text{Ac}_2\text{O}-\text{HCO}_2\text{H}$  followed by esterification into  $\text{Me}_2$  1':8'-dihydroxy-2:3:6:7-tetramethyl-1:8-di- $\beta$ -carbethoxyaminoethylbilidriene-4:5-dipropionate, m.p. 185°. 5'-Hydroxy-3:3'-dimethyl-4'- $\beta$ -aminoethylpyrromethene-4-propionic acid (VIII) and 1':8'-dihydroxy-2:3:6:7-tetramethyl-1:8-di- $\beta$ -acetamidoethylbilidriene-4:5-dipropionic acid are obtained as described for the isomerides. The latter substance is hydrolysed to the non-cryst. amine hydrochloride, which is transformed into biliverdin IIIa, m.p. 230° (Kofler). (VIII) and Me formylvinylneoxanthate in boiling  $\text{MeOH}-48\%$   $\text{HBr}$  afford  $\text{Me}_2$  1':8'-dihydroxy-1:3:6:7-tetramethyl-2-vinyl-8- $\beta$ -aminoethylbilidriene-4:5-dipropionate hydrobromide, hydrolysed and then transformed by  $\text{Zn}(\text{OAc})_2$  and  $\text{Me}_2\text{SO}_4$  into biliverdin IXa, m.p. 206–209°. (V) is converted by treatment with  $\text{HCN}-\text{HCl}$  in  $\text{CHCl}_3$  and then with  $\text{H}_2\text{O}$  into 5-hydroxy-5'-aldehyde-3':4'-dimethyl-3- $\beta$ -carbethoxyaminoethylpyrromethene-4'-propionic acid, m.p. 233°, which is condensed to  $\text{Me}_2$  1':8'-dihydroxy-1:3:6:7-tetramethyl-2:8-di- $\beta$ -carbethoxyaminoethylbilidriene-4:5-dipropionate, m.p. 210° (Kofler), transformed by conc.  $\text{HCl}$  at  $100^\circ$  into biliverdin IXa [Me ester, m.p. 199–200°, hydrolysed ( $\text{KOH}-\text{MeOH}$ ) and reduced ( $\text{Na}_2\text{S}_2\text{O}_4$ ) to bilirubin].

H. W.

**Action of sodium amalgam on position-isomeric, monoalkyl derivatives of 5-keto-3-thion-6-benzyl-1:2:4-triazine.** E. Cattelain (*Compt. rend.*, 1942, 214, 429–431).—2-Monoalkyl derivatives are not affected by  $\text{Na}-\text{Hg}$ , which cyclises  $\beta$ -alkylthiosemicarbazones of  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , the liberated alkali acting as a dehydrating agent. 3-Monoalkyl compounds give the 3:4- $\text{H}_2$ -derivatives without opening of the heterocyclic ring. 4-Monoalkyl derivatives give 1:6- $\text{H}_2$ -derivatives without rupture of the ring whereas the parent compound suffers ring opening between 4 and 5 and then adds 2 H at 1 and 6 yielding  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{H})\cdot[\text{NH}]_2\cdot\text{CS}\cdot\text{NH}_2$ . H. W.

**Diacylamino-1:3:5-triazines.**—See B., 1943, II, 7.

**Pyrazole nucleus. Transposition of bis-4:5'- into bis-4:4'-pyrazolone.** G. B. Crippa and R. Caracci (*Gazzetta*, 1941, 71, 574–580).—1-Phenyl-3-methyl-5-pyrazolone with  $\text{BzOH}$  at  $100^\circ$  (8–10 hr.) or  $\text{NH}_2\text{Ph}$  at  $180^\circ$  gives 4:5'-anhydro-bis-(1-phenyl-3-methyl-5-pyrazolone),  $\text{N}=\text{CMe}$   
 $\text{NPh}\cdot\text{CO}>\text{C}:\text{C}<\text{NPh}\cdot\text{N}$  (I), m.p. 258° (cf. Ionescu *et al.*, A., 1928, 74), which with  $\text{AcOH}$  forms a compound,  $\text{M}_2\text{AcOH}$ , m.p. 244°. With  $\text{AcOH}-\text{Br}$ , (I) gives its 4'-Br-derivative, m.p. 214°, with "pyrazole-blue,"  $\text{N}=\text{CMe}$   
 $\text{NPh}\cdot\text{CO}>\text{C}:\text{C}<\text{CMe}\cdot\text{N}$  (II), also obtained from, and reduced by  $\text{Zn}-\text{AcOH}$  to, 4:4'-bis-(1-phenyl-3-methyl-5-pyrazolone). The transposition from 4:5'- to 4:4'-structure on formation of (II) is attributed to enolisation of (I), which in fact gives ( $\text{Me}_2\text{SO}_4$ ) a Me ether, 5-methoxy-1-phenyl-4-(1'-phenyl-3'-methylpyrazolyl)-3-methylpyrazole, m.p. 130°, which with  $\text{Br}-\text{AcOH}$  gives only a 4'-Br-derivative, m.p. 93°, with no 4:4'-product of "pyrazole-blue" type. E. W. W.

**Quinoxaline cyanines.** I. A. H. Cook, J. Garner, and C. A. Perry (*J.C.S.*, 1942, 710–713).—Dimethylquinoxaline methiodide (I) in

$\text{C}_5\text{H}_5\text{N}$  with  $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  in  $\text{Ac}_2\text{O}$  gives 2-(1:3-dimethylquinoxaline)-1-(4-dimethylaminobenzene)dimethincyanine, m.p. 244° (methosulphate, m.p. 182–183°), which may also be prepared without the isolation of the methiodide; the corresponding -3-methyl-1-ethyl compound (ethosulphate, m.p. 170–171°) may also be similarly obtained. 1:3:3-Trimethyl-2-methyleneindoline- $\omega$ -aldehyde and (I) yield 2-(1:3-dimethylquinoxaline)-2-(1:3:3-trimethylindoline)trimethincyanine, m.p. 188°. Quinaldine methiodide and diphenylformamidine afford 2-anilinoethylquinoxaline methiodide (II), m.p. 256° (decomp.); with the appropriate reagents, 2-methylanilino-vinyl-benzoxazole ethiodide, m.p. 212°, -benzthiazole methiodide (III), m.p. 244°, and -quinoxaline methiodide, m.p. 271°, are similarly obtained. Of these three compounds, only (III) can be hydrolysed ( $\text{NaOH}$ ) to 1-methyl-2-methylenebenzthiazoline- $\omega$ -aldehyde, m.p. 99°. With  $\text{Ac}_2\text{O}-\text{NaOAc}$ , (I) and (II) give 2-(1:3-dimethylquinoxaline)-2-(1-methylquinoxaline)trimethincyanine, m.p.  $>360^\circ$ . 2-(1:3-Dimethylquinoxaline)-2-(1-methylbenzoxazole)trimethincyanine iodide, decomp.  $>300^\circ$ , may be obtained similarly without the isolation of the intermediate derivatives.  $\text{HCO}_2\text{Na}$  and (I) in  $\text{Ac}_2\text{O}$  when kept below  $20\text{--}25^\circ$  yield bis-2-(1:3-dimethylquinoxaline)trimethincyanine iodide, m.p. 204–205°, after treatment with  $\text{KI}$ .  $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHPh}$  with  $\text{Ac}_2$  followed by  $\text{Ac}_2\text{O}$  and  $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  in  $\text{C}_5\text{H}_5\text{N}$  and treated with  $\text{NaCl}$  gives 2-(1-phenyl-3-methylquinoxaline)-1-(4-dimethylaminobenzene)dimethincyanine chloride, decomp.  $\sim 320^\circ$ . By using the same amine with the appropriate aldehyde under specified conditions the following are obtained: 2-(1-phenyl-3-methylquinoxaline)- (acetate, m.p. 154°) and 2-(1-phenylquinoxaline)-2-(1:3:3-trimethylindoline)-trimethincyanine (iodide, m.p. 177°); bis-2-(1-phenyl-3-methylquinoxaline)trimethincyanine acetate, m.p. 161° (chloride, decomp.  $>300^\circ$ ); and 2-(1-phenylquinoxaline)-1-(4-dimethylaminobenzene)dimethincyanine iodide, decomp.  $>300^\circ$ . A strong bathochromic influence of the quinoxaline system is evident from the deep blue colour of the cyanines described. F. R. S.

**Exchange experiments with radioactive tracers.**—See A., 1943, I, 38.

**Condensations between methoxyacetonitrile and ketones. iso-Oxazole group.** C. Musante (*Gazzetta*, 1941, 71, 553–565).— $\text{OMe}\cdot\text{CH}_2\cdot\text{CN}$  (I) and  $\text{COMeEt}$  with  $\text{Na}$  in  $\text{Et}_2\text{O}$ , followed by dil.  $\text{H}_2\text{SO}_4$ , gives a mixture, b.p.  $92\text{--}97^\circ/21\text{--}22\text{ mm.}$ , probably of  $\text{OMe}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CH}_2\cdot\text{COEt}$  (II) and  $\text{OMe}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CHMeAc}$ , converted by hydrolysis or on keeping into a mixture of diketones, which with  $\text{N}_2\text{H}_4\text{--EtOH}$ , followed by aq.  $\text{KMnO}_4$  and conc.  $\text{HCl}$  gives pyrazole-3:5-dicarboxylic acid, showing the presence of the diketone corresponding to (II). Similarly (I) and  $\text{COPhMe}$  (III) give  $\beta$ -imino- $\gamma$ -methoxy-n-butyrophenone (IV), m.p. 27–30°, b.p.  $180^\circ/6\text{--}7\text{ mm.}$  ( $\text{Cu}$  salt, m.p. 188–190°), which with  $\text{FeCl}_3\text{--EtOH}$  gives a product, m.p. 156–157°. When heated with 20%  $\text{NaOH}$ , (IV) evolves  $\text{NH}_3$ , giving (III). With  $\text{NaOEt}-\text{NH}_2\text{OH}\cdot\text{HCl}$  in  $\text{EtOH}$ , (IV) gives 5-phenyl-3-methoxymethylisooxazole, b.p.  $180^\circ/28\text{--}29^\circ$  (oxidised by  $\text{AcO}_2\text{H}$  to the 3-carboxylic acid), formed by initial replacement of  $:\text{NH}$  by  $:\text{N}\cdot\text{OH}$ . With conc.  $\text{HCl}$  at  $160\text{--}170^\circ$ , (IV) yields 5-phenyl-3-chloromethylisooxazole, m.p. 47.5–48.5°, hydrolysed by 10%  $\text{KOH}$  to give (III).  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$  and (I) give  $\beta$ -imino- $\gamma$ -methoxy-n-butyro-p-methoxyphenone, m.p. 96–98° ( $\text{Cu}$  salt, m.p. 210°), which with  $\text{NH}_2\text{OH}$  gives 5(or 3)-p-anisyl-3(or 5)-methoxymethylisooxazole, m.p. 55°, oxidised by  $\text{AcO}_2\text{H}$  to  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ .  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{COMe}$  and (I) give  $\beta$ -imino- $\gamma$ -methoxy-n-butyro-p-bromophenone [ $\text{Cu}$  salt, m.p. 221° (decomp.)]. E. W. W.

**Sulphonamide derivatives of isooxazole.** C. Musante (*Gazzetta*, 1941, 71, 565–573).— $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$  and 4-amino-3:5-dimethyl-, -5- and -3-methyl-, and -3-phenyl-isooxazole (obtained by  $\text{SnCl}_2$  reduction of the 4- $\text{NO}_2$ -compound) at  $100^\circ$  give products which with aq.  $\text{HCl}$  yield respectively 4-p-anilinesulphonamido-3:5-dimethyl-, m.p. 193–194° ( $\text{Ac}$  derivative, m.p. 245–246°), -5-methyl-, m.p. 136–137° [ $\text{Ac}$ , m.p. 222–224° (darkening), and  $\text{Ac}_2$ , m.p. 189–190°, derivatives], -3-methyl-, m.p. 146–148° ( $\text{Ac}$  derivatives, m.p. 192°) (which with  $\text{NaNO}_2$  gives a product, darkening at  $200^\circ$ ), and -3-phenyl-isooxazole, m.p. 170–171°.  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$  and 3:5-dimethylisooxazole-4-sulphonyl chloride give 3:5-dimethylisooxazole-4-sulphon-p-aminoanilide, m.p. 167°. E. W. W.

**2-Thiolthiazolines.**—See B., 1943, II, 7.

**Raman spectra of thiazole and its mono- and di-substituted derivatives.**—See A., 1943, I, 31.

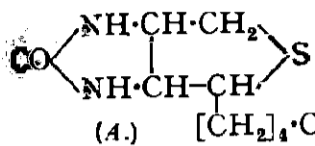
**Vapour pressure of hydrates of sulphathiazole sodium.** J. Crusellas (*J. Amer. Pharm. Assoc.*, 1942, 31, 157–158).—Data for commercial preps. of the mono- (I), sesqui- (II), and hexa-hydrate indicate that there are two structural modifications of (I) and that (II) is the most stable hydrate under average conditions. F. O. H.

**Action of phenylhydrazine on saccharin and thiosaccharin.** (Signa.) A. Mannessier-Mameli (*Gazzetta*, 1941, 71, 596–614).—Saccharin (I) and thiosaccharin (II) with  $\text{NHPh}\cdot\text{NH}_2$  (III) at room temp. give respectively the saccharinate, m.p. 130°, sweet, and thio-saccharinate (IV), m.p. 109–110°, bitter, of (III). In  $\text{AcOH}$ , or

at 140—145°. (II) and (III) give *saccharinphenylhydrazone* (V), m.p. 225° (decomp. 230°) (Bz derivative, m.p. 330—335°), not obtained under similar conditions from (I) and (III), which, however, give (V) at 160—180°, with *saccharinphenylimine* and *o*-amidodisulphonylbenzanilide. When heated above its m.p., (IV) gives (V).  $H_2O_2$  oxidises (V) to (I) and an amorphous product. At 235—240°, (V) gives *saccharinimine*, (I), and  $NH_2Ph$ . Its reducing properties suggest that (V) is tautomeric with 3-phenylhydrazino- $\psi$ -saccharin.

E. W. W.

**Condensation of phenanthrenequinone with the diaminocarboxylic acid derived from biotin.** K. Hofmann, G. W. Kilmer, D. B. Melville, and V. du Vigneaud (*J. Biol. Chem.*, 1942, 145, 503—509; cf. A., 1942, II, 387).—The diaminocarboxylic acid derived from biotin gives the *dibenzoquinoxaline* (I),  $C_{23}H_{20}O_2N_2S$ , m.p. 202—204°, and not the dihydroquinoxaline, suggesting that biotin possesses a 5-membered ring, and is probably A. The ultra-violet absorption spectra of the *dibenzo-*



*dihydroquinoxaline* (II), m.p. 183—185°, derived from 3:4-diaminotetrahydrothiophen differs from that given by (I). (II) heated at 200° and then sublimed at 200°/2 mm. gives the *dibenzoquinoxaline* derivative, m.p. 228—233°, the absorption spectrum of which is similar to that of (I).

A. T. P.

## VII.—ALKALOIDS.

**Erythrina alkaloids. XII. Chromatographic analyses of erysodine, erysovine, and "erysocene."** Technique for preparative isolation. K. Folkers and J. Shavel, jun. (*J. Amer. Chem. Soc.*, 1942, 64, 1892—1896; cf. A., 1942, II, 120).—These alkaloids are best separated by chromatography ( $Al_2O_3$ ;  $CHCl_3$ ; sometimes development by EtOH; technique described). Erysodine (I) and erysovine (II) are homogeneous, but "erysocene" (A., 1940, II, 332; cf. Gentile *et al.*, A., 1942, II, 275) is thus resolved into (I) and (II). Erysopine, (I), and (II) are isolated from *E. cubensis*, Wright, *E. pallida*, Britton and Rose, and *E. arborescens*, Roxb., (I) and (II) from *E. Folkersii*, Kruk. and Mold., *E. velutina*, Willd., and *E. excelsa*, Baker, and (I) from *E. Berteroana*, Urb.

R. S. C.

**Quinine sulphamate.** K. H. Stahl and R. A. Kuever (*J. Amer. Pharm. Assoc.*, 1942, 31, 154—156).—Quinine (1 mol.) with  $NH_2 \cdot SO_3H$  (1 or 2 mols.) in EtOH gives *quinine sulphamate*, m.p. 171—173° (decomp.), and *disulphamate*, m.p. 173—175° (decomp.). Photomicrographs of the crystals of the salts are given. F. O. H.

**Cinchona alkaloidal salts of sulphanilamide.**—See B., 1943, III, 21.

**Ergot alkaloids. XIX. Transformation of dl- and d-lysergic acid into 6:8-dimethylergolines.** R. G. Gould, jun., L. C. Craig, and W. A. Jacobs (*J. Biol. Chem.*, 1942, 145, 487—494; cf. A., 1939, II, 525).—*dl*-Lysergic acid, m.p. 251° (decomp.), and Na-BuOH give *dl-dihydrolysergic acid*, m.p. 290—300°; sublimation at 350°/25 mm. then yields the unsaturated *dl-lactam*,  $C_{16}H_{16}ON_2$ , m.p. 313—316° (cf. A., 1938, II, 384), hydrogenated ( $PtO_2$ -AcOH at room temp.) to the saturated *dl-lactam*,  $C_{16}H_{18}ON_2$ , m.p. 332—336° and 310—315° (possibly racemic modifications); the two forms are combined and reduced by Na-BuOH possibly to (mainly) 7-hydroxy-6:8-dimethylergoline, and sublimation of the product at 200°/0.2 mm. affords *dl-dehydro-6:8-dimethylergoline*, m.p. 182—186°, hydrogenated ( $PtO_2$ -AcOH) to *dl-6:8-dimethylergoline*, m.p. 227—229° (two cryst. forms), identical with the synthetic product. The structure of lysergic acid is thus confirmed. Optically active  $\alpha$ -dihydrolysergic acid is similarly converted into the unsaturated lactam, and thence ( $H_2$ ;  $PtO_2$ -EtOH) into the saturated *lactam*, m.p. 332—336° [some stereoisomeride (I), m.p. 300—308°, is also isolated], a dehydro-6:8-dimethylergoline, m.p. 155—157°, and 6:8-dimethylergoline, m.p. 246—248° (apparent change of cryst. form at 170°),  $[\alpha]_D^{25} -49^\circ$  in  $CHCl_3$ . (I) similarly affords a little 6:8-dimethylergoline, m.p. 234—238°. The unsaturated *lactam*,  $C_{16}H_{16}ON_2$ , obtained from  $\gamma$ -dihydrolysergic acid at 350°/25 mm. has m.p. 239—240°,  $[\alpha]_D^{20} -197^\circ$  in  $C_5H_5N$ .

A. T. P.

## VIII.—ORGANO-METALLIC COMPOUNDS.

**New heterocyclic systems.** F. G. Mann, F. G. Holliman, and D. R. Lyon (*Nature*, 1942, 150, 603).—*o*-Br $[(CH_2)_2C_6H_4CH_2Br]$  condenses readily with alkyl- or aryl-dichloroarsines in presence of metals to give stable 2-alkyl(aryl)-1:2:3:4-tetrahydroisoarsinolines. Less good yields of 2-aryldihydroisoarsindoles are obtainable by the use of *o*-xylylene dibromide.

A. A. E.

**Vital stains.**—See A., 1943, II, 31.

**Electrolysis of Grignard reagents. Short-lived free radicals in ethyl ether.** R. Pearson and W. V. Evans (*Trans. Electrochem. Soc.*, 1942, 82, Preprint 23, 257—264).—Hydrocarbons have been prepared by electrolysis of ethereal Grignard reagents and the ten-

dencies of the liberated free radicals to combine or to disproportionate have been determined. Me, if in sufficiently high concn., forms  $C_2H_6$ , but if the concn. is low Me attacks the solvent forming  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ , EtOH, and  $Pr^iOH$ . Et disproportionates whereas  $Pr^a$  both combines and disproportionates. Branching of the C chain decreases the combining tendency, probably by steric effect, whereas increase in C chain length increases this tendency. Bz,  $CH_2Ph$ , and cyclohexyl combine. The current efficiency is  $\sim 100\%$ . Possible reaction mechanisms are discussed. Mg aryl compounds have similarly been examined. The results support previous theories of the formation of free radicals by electrolysis.

C. R. H.

**Tetra-aryl-phosphonium, -arsonium, and -stibonium salts. II. Mechanism of their formation by the aluminium chloride reaction.** D. R. Lyon and F. G. Mann (*J.C.S.*, 1942, 666—671).— $AlCl_3$  and  $AsPh_3$  combine in  $CS_2$  to give *trichlorotriphenylarsinealuminium* (I),  $[AsPh_3 \rightarrow AlCl_3]$ , oxidised in PhBr by air to  $AsPh_3O$ . *Tetraphenylarsonium picrate* has m.p. 201—202°, and the *thiocyanate*, m.p. 268—270°. At 200° (I) and PhBr give the  $AsPh_4$  salt, without formation of by-products. The formation of (I) is confirmed by the prep. of mixed salts: *triphenyl-p-tolylarsonium iodide* ( $+H_2O$ , m.p. 186—187°), *thiocyanate* ( $+H_2O$ , m.p. 147—148°); *diphenyldi-p-tolylarsonium iodide* ( $+1.5H_2O$ , m.p. 194—195°); and *phenyltri-p-tolylarsonium iodide*, m.p. 205—206°, and *thiocyanate*, m.p. 143—144°. (I) is thermally stable to  $\sim 250^\circ$ . When (I) is prepared with impure  $AlCl_3$ ,  $C_6H_6$  is evolved and  $AsPh_4$  salt is produced.  $AlCl_3$  and  $AsPh_2Cl$  in  $CS_2$  give the unstable additive product, *trichlorodiphenylchloroarsinealuminium* (II), which, at 200°, gives  $AsPh_4Cl$  and As. When impure  $AlCl_3$  is used,  $C_6H_6$  is produced and less  $AsPh_4$ .  $AsPh_4$  is not produced by heating PhBr and (II). With  $AlCl_3$  and  $AsPhCl_2$ , *trichlorotris(phenyldichloroarsine)aluminium* is formed, a non-ionic compound containing 6-covalent Al; on heating  $AsCl_3$  and  $AsPh_2Cl$  are formed.  $C_6H_6$  and  $AsCl_3$  with  $AlCl_3$  give  $AsPhCl_2$ , which reacts as described. Thus the As ion can arise in only two ways: by the interaction of (I) and PhBr, and by the thermal decomp. of  $[AsClPh_2 \rightarrow AlCl_3]$ . The following are also described: *tri-o-tolylarsine hydroxyoxybromide*, m.p. 148—152°, *oxydibromide*, m.p. 232°, *oxydipicrate*, m.p. 169—171°, and *hydroxyoxyiodide*; *tetra-p-tolylarsonium iodide*, m.p. 253—255°, and *thiocyanate* ( $+H_2O$ ), m.p. 207—209°; *tetra-m-tolylarsonium iodide*, m.p. 155—156°; *tetra-p-tolylphosphonium iodide*, m.p. 260—264°, and the *m*-compound, m.p. 175—176°; and *tetraphenylphosphonium thiocyanate*.

F. R. S.

## IX.—PROTEINS.

**Analysis and minimum mol. wt. of  $\beta$ -lactoglobulin.** E. Brand and B. Kassell (*J. Biol. Chem.*, 1942, 145, 365—378).—The min. mol. wt. of  $\beta$ -lactoglobulin (I) (42,000) obtained from the distribution of the S-containing  $NH_2$ -acids and from the arginine content agrees with the mol. wt. in solution (41,600). (I) contains 364(+3)  $NH_2$ -acid residues + 1 to 6 terminal  $NH_2$ -acids. 1 mol. contains the following residues: cysteine 4, half-cysteine 8 (i.e., 4 S-S linkings), methionine 9, tryptophan 4, tyrosine 9, arginine 7, threonine 21, serine  $\sim 15$ , amide groups 22, histidine 4—6, and lysine 31—36. The side-chains of (I) contain  $>45$  OH and it is suggested that these contribute to the cohesion of the mol. by H bridges through  $H_2O$  mols.

J. E. P.

**X-Ray diffraction studies of iodinated amino-acids and proteins.**—See A., 1943, I, 8.

**Phosphopeptones of caseinogen (lactotyris).**—See A., 1942, III, 902.

**Ultracentrifugal isolation from lung tissue of a macromolecular protein component with thromboplastic properties.**—See A., 1943, III, 84.

## X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

**Purification and chemistry of penicillin.** J. R. Catch, A. H. Cook, and I. M. Heilbron (*Nature*, 1942, 150, 633—634).—By chromatography from an org. solvent on a column consisting of a  $H_2O$ -retentive support associated with an inorg. base, penicillin (I) is recovered quantitatively and manifold concn. is easily accomplished. The yellow Sr salt,  $C_{24}H_{34}O_{11}NSr$ , has no measurable optical activity. Dil. acid, alkali, or moist org. bases afford by fission a  $H_2O$ -sol. acid, an insol. pigment ( $C_{16}H_{20}O_6$  or possibly  $C_{16}H_{18}O_5 \cdot H_2O$ ), MeCHO, and a little  $\alpha\beta$ -unsaturated aldehyde,  $C_7H_{12}O$  but no  $CO_2$ . Reduction of (I) with Al-Hg affords as hydrolysis product an insol. compound,  $C_{16}H_{20}O_5$ . Ozonolysis of the pigment affords MeCHO, whilst degradation with alkaline permanganate affords  $<3$  mols. of  $H_2C_2O_4$ .

A. A. E.

**Beech bark (*Fagus silvatica*).**—See A., 1943, II, 39.

## XI.—ANALYSIS.

**Standardisation of chromatographic analysis.** A. L. LeRosen (*J. Amer. Chem. Soc.*, 1942, **64**, 1905—1907).—Chromatography may be put on a quant. basis by use of the terms,  $S$  = length of absorbent column containing a unit vol. of solvent/length of empty tube required to contain the same vol. of solvent,  $V_0$  = the const. rate of flow of the solution (the initial rate is abnormally fast), and  $R$  = rate of movement of an adsorbate zone relative to that of the developing solvent. This is illustrated for various carotenoids on  $\text{Ca}(\text{OH})_2$  developed by  $\text{C}_6\text{H}_6$  and is used successfully to predict the behaviour of some mixtures. R. S. C.

**Determination of ammonia by a diffusion method.**—See A., 1943, I, 41.

**Kjeldahl distillation without absorbing acid.**—See A., 1943, I, 41.

**Sulphur in organic compounds containing nitrogen and halogen. Acidimetric micro-determination.** E. L. Brewster and W. Riemann (*Ind. Eng. Chem. [Anal.]*, 1942, **14**, 820—821).—The  $\text{H}_2\text{SO}_4$  resulting from the combustion in  $\text{O}_2$  is evaporated in a stream of purified air,  $\text{HNO}_3$  and  $\text{HCl}$  being removed by evaporation. Apparatus and procedure are detailed. J. D. R.

**Qualitative and quantitative analysis of hydrocarbon mixtures by means of their Raman spectra.** D. H. Rank, R. W. Scott, and M. R. Fenske (*Ind. Eng. Chem. [Anal.]*, 1942, **14**, 816—819).—A linear relation between the relative intensity of the Raman lines compared with an internal standard and the vol. concn. is shown for six binary mixtures of hydrocarbons, one of which is an azeotropic mixture of min. b.p. This linear relationship is general for mixtures of nearly all hydrocarbons within the limits set for the determination of intensities of Raman lines by means of photographic plates. Scattering coeffs. are described and vals. for this const. are given for a series of hydrocarbons. Qual. and quant. analysis of hydrocarbon mixtures by means of Raman spectra could be substituted for infra-red analysis in cases where components of the mixtures contain appreciable % of the constituents to be determined. J. D. R.

**Identification of alcohols and alkyl hydrogen sulphates with *S*-benzylthiuronium chloride.** R. K. Bair and C. M. Suter (*J. Amer. Chem. Soc.*, 1942, **64**, 1978).—Alcohols are converted by  $\text{ClSO}_3\text{H}$ -dioxan and then *S*-benzylthiuronium chloride in  $\text{H}_2\text{O}$  or aq.  $\text{EtOH}$  into  $\text{Pr}^a$ , m.p. 111.5—112.5°,  $\text{Pr}^b$ , m.p. 142—143°,  $\text{Bu}^a$ , m.p. 100—101°,  $\text{CHMeEt}$ , m.p. 117—119°,  $\text{Bu}^b$ , m.p. 136—137°, *n*-amyl, m.p. 85—86°, *n*-hexyl, m.p. 85—86°, *n*-heptyl, m.p. 77—79°, *n*-octyl, m.p. 42—70°, *n*-decyl, m.p. 73—75°, *n*-dodecyl, m.p. 74—76°, *myristyl*, m.p. 87—88°, *cyclohexyl*, m.p. 163—164°, *bornyl*, m.p. 174—175°, and *menthyl*, m.p. 149—150°, *S*-benzylthiuronium sulphate and ethylene di-*S*-benzylthiuronium disulphate, m.p. 180—181°.  $\text{NaAlkSO}_4$  are similarly identified.  $\text{MeOH}$  and  $\text{EtOH}$  do not give cryst. salts. *S*-*p*-Chlorobenzylthiuronium chloride gives waxy salts. M.p. are corr. R. S. C.

**Effect of formaldehyde on the volatilisations of ammonia, mono-, di-, and tri-methylamine.** G. J. Benoit, jun., and E. R. Norris (*Ind. Eng. Chem. [Anal.]*, 1942, **14**, 823—825).— $\text{CH}_2\text{O}$  renders  $\text{NH}_3$  almost completely non-volatile at room temp., but has no effect on the recovery of  $\text{NMe}_3$ . It does not completely prevent the volatilisation of  $\text{NH}_2\text{Me}$  and  $\text{NHMe}_2$ . When  $\text{NHMe}_2$  and  $\text{NH}_2\text{Me}$  are distilled in presence of  $\text{CH}_2\text{O}$  anomalies are observed which in the case of  $\text{NHMe}_2$  are probably due to  $\text{MeOH}$  present in the aq.  $\text{CH}_2\text{O}$ . J. D. R.

**Micro-determination of urea-nitrogen.** J. C. Bock [with F. A. Kordecki] (*J. Biol. Chem.*, 1941, **140**, 519—523).—A very simple but accurate micro-method is described. 0.5 c.c. of blood is treated with urease in presence of  $\text{Na}_2\text{CO}_3$ , and the liberated  $\text{NH}_3$  is absorbed in 0.1N- $\text{HCl}$  and determined by nesslerisation. The method is applicable to determination of urea-N in urine provided that  $\text{NH}_3$ -N is determined by the same method. J. N. A.

**Derivatives in the indane group as reagents for amines. IV. Methylbindone.** G. Wanag (*Z. anal. Chem.*, 1942, **123**, 292—305).—In glacial  $\text{AcOH}$  a green coloration is given by aromatic primary mono-, di- (not *o*-), tri-, and tetra-amines ( $>2 \text{NH}_2$  in one ring).  $\cdot\text{NO}_2$  and  $\cdot\text{SO}_3\text{H}$ , but not  $\cdot\text{Hal}$ ,  $\cdot\text{OH}$ ,  $\cdot\text{CO}$ , or  $\cdot\text{CO}_2\text{H}$ , interfere. The reaction is also given by  $\text{NPhR}$  ( $\text{R} \neq \text{Me}, \text{Et}$ ), *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NHR}$ ,  $\text{NPhR}_2$  (not  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NR}_2$ ),  $\text{C}_{10}\text{H}_7\cdot\text{NHR}$ ,  $\text{C}_{10}\text{H}_7\cdot\text{NMe}_2$ , *sec.*, purely aromatic amines with  $\text{Ph}$ ,  $\text{C}_6\text{H}_4\text{Me}$ , and  $\alpha\text{-C}_{10}\text{H}_7$  radicals,  $\text{NPh}_2\text{Et}$ , and  $\text{NPh}_2\text{CH}_2\text{Ph}$ . A. A. E.

**Photometric determination of arginine.** E. Brand and B. Kassell (*J. Biol. Chem.*, 1942, **145**, 359—364).—The intensity of the colour developed by arginine (I) in the Sakaguchi reaction (Weber, A.,

1930, 755) decreases linearly with increasing amounts of (I), and the inhibition of colour development by  $\text{NH}_3$  and by histidine likewise follows a linear course. Extrapolation to zero concn. yields the same colour value per unit wt. of (I). The (I) content of a protein is determined by estimating the apparent (I) contents of different amounts of a hydrolysate and then extrapolating to zero protein concn. The (I) content of cryst. proteins is: swine pepsin (0.96%, 2 residues per mol.), trypsinogen (1.61%), chymotrypsinogen (2.83%, 6 residues per mol.),  $\beta$ -lactoglobulin (2.87%, 7 residues per mol.), trypsin (3.27%), ribonuclease (5.16%), horse serum-albumin A (5.49%, 22 residues per mol.), horse serum-albumin B (5.52%, 22 residues per mol.), human serum-albumin (6.30%, 25 residues per mol.). J. E. P.

**Determination of both cystine and cysteine in mixtures.** M. X. Sullivan, W. C. Hess, and H. W. Howard (*J. Biol. Chem.*, 1942, **145**, 621—624).—Cystine (I) and cysteine (II) when determined by the  $\text{CN}^-(\text{I})$  method are equiv., mol., for mol., in chromogenic val., deviations being due to impurity in (II), irregular  $\text{H}_2\text{O}$  content, or to oxidation. When determined by the amalgam-cyanide procedure, (I) and (II) are equiv. in chromogenic val. mg. for mg., since 1 mol. of (I) gives 2 mols. of (II). (I) and (II) can be determined, either singly or in mixtures. A. T. P.

**Colorimetric micro-method for determination of cystine and cysteine.** B. Vassel (*J. Biol. Chem.*, 1941, **140**, 323—336).—The method is based on formation of a blue colour by heating cystine (I) or cysteine (II) or both in acid solution with  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$  in presence of  $\text{FeNH}_4(\text{SO}_4)_2$ , and determination of the % absorption at 580 m $\mu$ . by a spectrophotometer. The method is applicable to 0.01—0.20 mg. of (I) or (II) per c.c. of solution (error  $\pm 3\%$ ). The formation of the blue colour depends on a SH and a primary  $\text{NH}_2$ , which are separated by two  $\text{CH}_2$ . Reduced glutathione and homocystine do not give the blue colour but they interfere with determination of (I) by causing reduction of the blue to a leuco-compound. Ascorbic acid and tyrosine have no effect on the determination, but when the former is added after formation of the blue colour, it causes reduction to the leuco-compound. J. N. A.

**Colour reactions of phenols.** A. Steigmann (*J.S.C.I.*, 1942, **61**, 180).—Monohydric phenols and resorcinol give blue or bluish-green colorations with Na  $\beta$ -naphthaquinonesulphonate in presence of  $\text{NH}_3$  in aq. solution. *p*-Substituted phenols give a very weak reaction or none. Blue and violet colours are also given by certain phenols when oxidised together with  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHPH}$  or other *p*-phenylenediamines, preferably by chloramine-T; here again *o*- and *m*-phenols give the strongest reactions. The characteristic yellow Ag and red-brown Cu salt of  $\text{C}_6\text{Cl}_5\cdot\text{OH}$  are described.

**Determination of purines.** G. H. Hitchings and C. H. Fiske (*J. Biol. Chem.*, 1941, **140**, 491—499; cf. A., 1941, II, 276).—The protein-free tissue filtrate containing 3—4 mg. of purine-N is diluted to  $\sim 30$  c.c. in a 50 c.c. conical-tip centrifuge tube and neutralised to phenolphthalein. After heating to 100° the purine bases are pptd. by addition of 0.8 c.c. of saturated aq.  $\text{NaHSO}_3$  and 1 c.c. of 10% aq.  $\text{CuSO}_4$ . The ppt. is centrifuged after 3 min., and washed twice with 10-c.c. portions of hot  $\text{H}_2\text{O}$ . The ppt. is suspended in 3 c.c. of 3N- $\text{HCl}$  and boiled cautiously. After addition of 15 c.c. of  $\text{H}_2\text{O}$  the mixture is heated on the steam-bath while  $\text{H}_2\text{S}$  is passed in for  $\sim 3$  min. The mixture is then cooled, diluted to 25 c.c., filtered, and N determined in an aliquot by the micro-Kjeldahl method. J. N. A.

**Determination of sodium phenylethylbarbiturate.** E. A. Kocsis and E. Kovács (*Z. anal. Chem.*, 1942, **124**, 40—42).—The aq. Na phenylethylbarbiturate (I) is pptd. by an excess of 0.1N- $\text{AgNO}_3$ . The ppt. is collected on a No. 1 G4 Jena crucible (not paper), and the excess of Ag<sup>+</sup> in the filtrate determined by Volhard's method using 0.1N-KCNS. Ag<sup>+</sup> can be determined by adding excess of (I), followed by excess of 0.1N- $\text{AgNO}_3$ , and then titration of excess Ag<sup>+</sup> with 0.1N-KCNS. L. S. T.

**Capillary analysis of some important opium alkaloids in filtered ultra-violet light.** E. A. Kocsis and Z. Holló (*Z. anal. Chem.*, 1942, **124**, 35—40).—The colours given by 1% aq. solutions of morphine, codeine, thebaine, papaverine, narcotine, and narceine on Schleicher & Schüll No. 602 filter-paper in daylight and in ultra-violet light are tabulated and discussed. L. S. T.

**Relation of alkaloidal to inorganic chemistry.**—See A., 1943, I, 42.

**Determination of arsenic in organic arsenical compounds.** F. B. Rodman and H. N. Wright (*J. Amer. Pharm. Assoc.*, 1942, **31**, 200—202).—The Lehmann volumetric method (U.S.P. X) gives significantly lower results than the Treadwell-Hall gravimetric method. J. E. P.

## A., II.—Organic Chemistry

MARCH, 1943.

## I.—ALIPHATIC.

**Reaction of hydrogen atoms with isobutane.** W. H. White, C. A. Winkler, and B. J. Kenalty (*Canad. J. Res.*, 1942, 20, B, 255—264).—The reaction of H atoms with *iso*-C<sub>4</sub>H<sub>10</sub> has been investigated by the Wood-Bonhoeffer discharge tube method at 50—250°; the activation energy of the reaction is 10.5 ± 1.5 kg.-cal. The nature of the products at a given temp. depends on the concn. of H atoms present. With low at. concn. (5—9%) CH<sub>4</sub> is essentially the only product at <170°. At 250° the yield of C<sub>2</sub>H<sub>6</sub> is ~ half that of CH<sub>4</sub>. With higher at. concn. (14—24%) C<sub>2</sub>H<sub>6</sub> is formed in appreciable quantities at 140—170° and exceeds the CH<sub>4</sub> content at 250°. Small amounts of C<sub>3</sub>H<sub>8</sub> are formed at the higher temp. The results at low temp. appear to be explained satisfactorily by assuming a primary dehydrogenation reaction, *iso*-C<sub>4</sub>H<sub>10</sub> + H → C<sub>4</sub>H<sub>9</sub> + H<sub>2</sub>, followed by a series of "atomic cracking" reactions. To account for the behaviour at higher temp., additional secondary reactions, involving decomp. of radicals and their reaction with mol. H<sub>2</sub>, are assumed. H. W.

**Reactions of alkyl halides with hydrogen halides.**—See A., 1943, I, 65.

**Hydrogenation of disubstituted acetylenes.** K. W. Greenlee and W. C. Fernelius (*J. Amer. Chem. Soc.*, 1942, 64, 2505).—*trans*-Hydrogenation of acetylenes (Campbell *et al.*, A., 1941, II, 81) is explained by the mechanism:  $\text{Na} \rightleftharpoons \text{Na}^+ + e^-$ ;  $\text{CR}:\text{CR} + e^- \rightarrow \text{C}^-\text{R}:\text{CR} \rightarrow (+e^-)(\text{C}^-\text{R})_2$ ;  $(\text{C}^-\text{R})_2 + 2\text{NH}_3 \rightarrow (\text{CHR})_2 + 2\text{NH}_2^-$ . R. S. C.

**Addition of hydrogen fluoride to the triple linking.** A. V. Grosse and C. B. Linn (*J. Amer. Chem. Soc.*, 1942, 64, 2289—2292).—HF and C<sub>2</sub>H<sub>2</sub> do not react at -70° to 300°/1 atm. but at room temp./13 atm. give a 35 : 65 mixture of CH<sub>2</sub>:CHF and CHMeF<sub>2</sub> with much polymeride. Other acetylenes react similarly with HF (excess) at -70° to -55°/1 atm. Thus CH<sub>2</sub>:CMe gives CMe<sub>2</sub>F<sub>2</sub> (61%), m.p. -104.8°, b.p. -0.1°, and some polymeric product, C<sub>6</sub>H<sub>13</sub>F. CH<sub>2</sub>:CEt or (CMe)<sub>2</sub> gives CMeEtF<sub>2</sub>, m.p. -116.9°, b.p. 30.4—30.6°/747 mm. CH<sub>2</sub>:CPr<sup>a</sup> gives CMePr<sup>a</sup>F<sub>2</sub>, b.p. 58.2—58.8°/749 mm. CH<sub>2</sub>:CBu<sup>a</sup> and (CEt)<sub>2</sub> give ββ-, b.p. 86.0—86.2°/750 mm., and γγ-difluoro-*n*-hexane (76%), b.p. 86°/742 mm., respectively. CH<sub>2</sub>:C-C<sub>5</sub>H<sub>11</sub>-*n* gives ββ-difluoro-*n*-heptane, b.p. 111.7—111.9°/749 mm. R. S. C.

**Constitution of piryrene.**—See A., 1943, I, 54.

**Structure of co-polymerides of vinyl chloride and vinyl acetate.** C. S. Marvel, G. D. Jones, T. W. Mastin, and G. L. Schertz (*J. Amer. Chem. Soc.*, 1942, 64, 2356—2362).—CH<sub>2</sub>:CHCl (I) and CH<sub>2</sub>:CH·OAc co-polymerise to mixed chains, but those formed initially preferentially remove the (I). Thus, after complete polymerisation, the product is heterogeneous. Hydrolysis of the polymeride by HCl-H<sub>2</sub>O-EtOH gives a chlorohydrin, unaffected by HIO<sub>4</sub>, indicating head-to-tail union. This union is less clearly shown by dehalogenation, which is quantitatively rather erratic and may give cyclopropane units since the products decolorise Br-CCl<sub>4</sub> but not KMnO<sub>4</sub>-COMe<sub>2</sub>. R. S. C.

**Polyene series. VI. Preparation of ethynylcarbinols from αβ-unsaturated aldehydes.** E. R. H. Jones and J. T. McCrombie (*J.C.S.*, 1942, 733—735).—C<sub>2</sub>H<sub>2</sub> is passed into liquid NH<sub>3</sub> and Na added gradually; addition of PhCHO-Et<sub>2</sub>O, with continuous introduction of C<sub>2</sub>H<sub>2</sub> (3 hr.), gives (cf. Campbell *et al.*, A., 1939, II, 46) CH<sub>2</sub>:C·CHPh·OH, m.p. 22°, b.p. 115—116°/16 mm. (82.5% yield) [*phenyl*-, m.p. 81—82°, *p*-nitrophenyl-, m.p. 132°, and β-naphthylurethane, m.p. 120°; *H* phthalate, m.p. 98—99°; acetate (Ac<sub>2</sub>O at 100—115°), b.p. 124°/18 mm.]. CHMe:CH·CHO similarly affords CH<sub>2</sub>:C·CH(OH)·CH:CHMe (50—65%), b.p. 154—156°, 75°/24 mm. (Hg compound, m.p. >360°; *phenyl*-, m.p. 65°, and β-naphthylurethane, m.p. 89°; acetate, b.p. 110—112°/100 mm.), hydrogenated (Pd-C in MeOH) to CH<sub>2</sub>EtPr·OH (*phenylurethane*, m.p. 49—50°), oxidised to COEtPr (2 : 4-dinitrophenylhydrazones, new m.p. 134—135°). CH<sub>2</sub>:CH·CHO gives CH<sub>2</sub>:C·CH(OH)·CH:CH<sub>2</sub> (36%), b.p. 83.5—84.5°/150 mm. (*phenyl*-, m.p. 37°, and α-naphthylurethane, m.p. 127.5—128.5°; acetate, b.p. 87—88°/100 mm.), reduced by H<sub>2</sub>-PtO<sub>2</sub>-Et<sub>2</sub>O to CH<sub>2</sub>Et<sub>2</sub>·OH [α-naphthylurethane, m.p. 90—91° (lit. 71—72°)]. CMe<sub>2</sub>:CH·CHO yields isobutenylacetylenylcarbinol (50%), b.p. 110—113°/100 mm. (*phenyl*-, m.p. 58—59°, and β-naphthylurethane, m.p. 76°), reduced (H<sub>2</sub>-PtO<sub>2</sub>-AcOH) to

CH<sub>2</sub>EtBu<sup>β</sup>·OH. CHPr:CEt·CHO gives CH<sub>2</sub>:C·CH(OH)·CEt:CHPr (80%), b.p. 96.5—97°/14 mm. (α-naphthylurethane, m.p. 57—58°). Tiglic aldehyde (CHMe:CMc·CHO) yields δ-methylhex-Δ<sup>δ</sup>-en-Δ<sup>α</sup>-inen-γ-ol (75%), b.p. 96—97°/50 mm. (α-naphthylurethane, m.p. 105°). Furfuraldehyde or CHPh:CH·CHO gives 2-furyl- (65%), b.p. 83—85°/2 mm., or styryl-acetylenylcarbinol (2%), m.p. 66—67°, respectively. Light absorption data are recorded and active H (Zerevitinov) determined (a temp. of 90° is needed before reaction with acetylenic H is complete). A. T. P.

**Polyene series. VII. Carbinols from propargyl acetal.** I. M. Heilbron, E. R. H. Jones, and H. P. Koch (*J.C.S.*, 1942, 735—737; cf. preceding abstract).—CH<sub>2</sub>:C·CH(OEt)<sub>2</sub> and MgEtBr-Et<sub>2</sub>O, followed by EtCHO at 20°, give ζζ-diethoxy-Δ<sup>δ</sup>-hexinen-γ-ol (I) (40%), b.p. 107°/3 mm., the γ-Me derivative (II), b.p. 88°/3 mm., of which is similarly prepared using COMeEt. CH<sub>2</sub>Ph·COMe gives εε-diethoxy-α-phenyl-β-methyl-Δ<sup>γ</sup>-pentinen-β-ol (III). (I), (II), and (III) contain 1 active H and are characterised by treatment with NH<sub>2</sub>·CO<sub>2</sub>Et in dil. HCl, thus affording the diurethano-derivatives [*i.e.*, (NH·CO<sub>2</sub>Et)<sub>2</sub> replacing (OEt)<sub>2</sub>], m.p. 143°, 111°, and 130°, respectively. (II), H<sub>2</sub> (1 mol.), and Pd-CaCO<sub>3</sub> in MeOH afford a complex mixture, from which EtOH and 2-ethoxy-5-methyl-5-ethyl-2 : 5-dihydrofuran (IV), b.p. 151°, 46°/19 mm., and a substance, C<sub>14</sub>H<sub>21</sub>O<sub>2</sub>·OEt, b.p. 110°/4 mm., are isolated. (IV) and 2 : 4 : 1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·NH·NH<sub>2</sub> in HCl-EtOH yield the 2 : 4-dinitrophenylhydrazone, m.p. 194°, of γ-methylsoraldehyde, formed by simultaneous hydrolysis and dehydration; semicarbazide acetate in hot H<sub>2</sub>O converts (IV) into the semicarbazone, m.p. 169° (small yield), of OH·CMeEt·CH:CH·CHO. Semihydrogenation of (III) also gives a poor yield of a dihydrofuran. A. T. P.

**Electrical properties of polymethyl acrylate, methacrylate, and α-chloroacrylate, and polychlorethyl methacrylate.**—See A., 1943, I, 51.

**Fats containing fatty acids with odd numbers of carbon atoms. II—IV.**—See A., 1943, III, 46, 131.

**Antioxidants and autoxidation of fats. XIV. Isolation of new antioxidants from vegetable fats.** C. Golumbic (*J. Amer. Chem. Soc.*, 1942, 64, 2337—2340; cf. B., 1941, II, 348).—When autoxidation of cottonseed, soya-bean, or mixed hydrogenated vegetable fats has proceeded until tocopherols are all destroyed, there remains a different type of antioxidant. The latter can be conc. by chromatography, best using activated Al<sub>2</sub>O<sub>3</sub> and the Et esters (prep. by HCl-EtOH) in light petroleum. The absorption spectra (max. at 560—570 mμ.), inactivation by reductive acetylation to stable, colourless oils, decolorisation to readily oxidisable products, ready reaction with *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> to fluorescent (ultra-violet) products, instability to alkali, red colour, and lack of vitamin-E activity resemble the properties of chroman-5 : 6-quinones. These red compounds are formed from colourless phenolic precursors in the fats. R. S. C.

**Diastereoisomerism of the θλ-trihydroxystearic acids. Geometric configurations of ricinoleic and ricinelaidic acids.** J. P. Kass and S. B. Radlove (*J. Amer. Chem. Soc.*, 1942, 64, 2253—2257).—Structures assigned below follow established rules (cf. A., 1939, II, 297) and confirm the *cis*-configuration of ricinoleic (I) and *trans*-configuration of ricinelaidic acid (II). Many data in the literature are corr. Configurations +++ etc. refer to C<sub>λ</sub>, C<sub>ν</sub>, and C<sub>θ</sub>, respectively. (I) (prep. from castor oil modified; best by way of Me esters) with KMnO<sub>4</sub>-KOH-H<sub>2</sub>O at 0° gives θλ-trihydroxystearic acid, α-, m.p. 109.6—112.4°, [α]<sub>D</sub><sup>23</sup> -2.9° in EtOH, -6.6° in AcOH, and β-form, m.p. 137.6—138.2°, [α]<sub>D</sub><sup>23</sup> -3.9° in EtOH, -11.6° in AcOH, which are the +-+ and --+ acids or vice versa; (II) gives similarly θλ-trihydroxystearic acid, γ-, m.p. 86.8—87.4°, [α]<sub>D</sub><sup>23</sup> +19.1° in EtOH, +21.8° in AcOH, and δ-form, m.p. 109.4—110.4°, [α]<sub>D</sub><sup>23</sup> -26.6° in EtOH, -38.7° in AcOH, which are +++ and --- acids, respectively. Conversely, H<sub>2</sub>O<sub>2</sub>-AcOH converts (I) into the γ- and δ-acids and (II) into the α- and β-acids. R. S. C.

**Organic acids of leaves of *Bryophyllum calycinum*. Identity of "crassulacean malic acid" with isocitric acid.**—See A., 1943, III, 150.

**Reaction of ninhydrin with ascorbic acid and other endiol compounds. Decarboxylation of dehydroascorbic acid.** E. S. West and R. E. Rinehart (*J. Biol. Chem.*, 1943, 146, 105—108).—Ninhydrin

(I) (2 mols.) and ascorbic acid (II) (1 mol.) at room temp., or more quickly on warming, give hydrindantin (III),  $C_{18}H_{10}O_6$ , also obtained from (I) and  $H_2S$  (cf. Ruhemann, *J.C.S.*, 1911, 99, 792, 1306). Reductone or dihydroxymaleic acid gives a similar ppt. Oxidation of (II) by (I) apparently stops at the stage of dehydroascorbic acid (IV); (IV) and (I) do not give (III).  $CO_2$  formed in the reaction (I) + (II) is probably due to decarboxylation of (IV), possibly involving hydrolysis of the lactone bridge, with formation of *l*-xylosone. At least part of the metabolism of (II) in the body may involve oxidation to (IV), followed by decarboxylation.

A. T. P.

**Photometric method for determining ascorbic acid.**—See A., 1943, III, 191.

**Photochemical decomposition of methyl *n*-butyl ketone.**—See A., 1943, I, 66.

**Synthesis of  $\alpha$ -amino-acids from substituted acetoacetic esters.** K. E. Hamlin, jun., and W. H. Hartung (*J. Biol. Chem.*, 1942, 145, 349–359).—The synthesis of  $\alpha$ - $NH_2$ -acids by nitrosating the respective substituted acetoacetic ester in 85%  $H_2SO_4$  with  $BuO\cdot NO$  at  $5^\circ$  to  $0^\circ$ , followed by hydrolysis by aq.  $NaOH$  of the  $\alpha$ -oximino-ester to the acid, and then hydrogenation at room temp./10 atm., using  $Pd-C$  (2 mol. equiv. of  $HCl$  in  $EtOH$ ), is described; the method is general. The  $\alpha$ -oximino-ester can be similarly reduced, followed by hydrolysis of the  $NH_2$ -acid ester. Alanine,  $\alpha$ -amino-butyric acid, norvaline (Bz derivative, m.p.  $153.5^\circ$ ), nor- and *iso*-leucine, aspartic acid, glutamic acid, phenylalanine, and *O*-methyl-tyrosine ( $HCl$  at  $180^\circ$  gives tyrosine) are prepared. The following are described:  $\alpha$ -oximino-acids,  $R\cdot C(N\cdot OH)\cdot CO_2H$  [ $R = Me$ , m.p.  $182^\circ$  (decomp.);  $Et$ , m.p.  $155^\circ$  (decomp.);  $Pr$ , m.p.  $145^\circ$  (decomp.);  $Bu$ , m.p.  $137^\circ$  (decomp.);  $CHMeEt$ , m.p.  $145^\circ$  (decomp.);  $CH_2Ph$ , m.p.  $168^\circ$  (decomp.); *p*- $OMe\cdot C_6H_4\cdot CH_2$ , m.p.  $157^\circ$  (decomp.)], and -esters,  $R\cdot C(N\cdot OH)\cdot CO_2Et$  [ $R = Me$ , m.p.  $96^\circ$ ;  $CH_2\cdot CO_2Et$ , an oil;  $[CH_2]_2\cdot CO_2Et$ , m.p.  $82^\circ$ ]. Photomicrographs of the  $NH_2$ -acids are reproduced.

A. T. P.

**Poly-condensation of  $\alpha$ -amino-acid esters.** Poly-condensation of (I) glycine esters, (II) alanine ethyl ester. M. Frankel and E. Katchalski (*J. Amer. Chem. Soc.*, 1942, 64, 2264–2268, 2268–2271).—I. Average degrees of polymerisation are denoted by numerical prefixes. Passage of  $N_2$  or  $H_2$  through  $NH_2\cdot CH_2\cdot CO_2Et$  (I) at room temp. gives a 20-polymeride, decomp.  $\sim 280$ – $300^\circ$ , quantitatively hydrolysed by boiling 10%  $H_2SO_4$  to glycine; subsequent contact with air gives a 25-polymeride; use of  $O_2$  gives a 16-polymeride. In xylene at room temp. (3 months), (I) gives a 12-polymeride or, at the b.p. (8 hr.) and then room temp. (2 months), a 13-polymeride. In  $C_6H_6$  at room temp. (70 days), (I) gives a 1:1 mixture of 4-polymeride and anhydride, but at the b.p. (7 hr.) and then room temp. (70 days) gives a 17-polymeride (quantitatively hydrolysed by 25%  $HCl$ ). Similar experiments with  $NH_2\cdot CH_2\cdot CO_2Me$  (modified prep.) give 18-, 30-, 27-, and 35-polymerides.  $NH_2\cdot CH_2\cdot CO_2Bu^t$  gives a 10-polymeride. Subsequent heating at  $130^\circ$  gives still higher polymerides, e.g., the 20- and 16-polymeric  $Et$  esters give up to a 42-polymeride and the 30-polymeric  $Me$  ester gives a 110-polymeride. The polymerides are isolated by removing impurities in hot  $H_2O$  (picric acid and biuret tests on washings negative); the chain-length is determined by the  $OMe$  content.

II.  $NH_2\cdot CHMe\cdot CO_2Et$  at room temp./15 mm. gives after 5 months a tetrapeptide (hygroscopic hydrochloride), alanine anhydride, and a 10-polymeric  $Et$  ester; at  $40^\circ$  it gives a 16-polymeride, at  $80^\circ$  a 14-polymeride, converted at  $150^\circ$  gradually into a 23-polymeride and quantitatively hydrolysed by  $HCl$ . Unlike the glycine polymerides, these polymerides are sol. in  $H_2O$  and are isolated as residues after "mol." sublimation of other products.

R. S. C.

**Sodium bismuth triglycollamate.** R. A. Lehman and R. C. Sproull (*J. Amer. Pharm. Assoc.*, 1942, 31, 190–192).— $CH_2Cl\cdot CO_2H$  is converted into triglycollamic acid in 60% yield; this gives *BiH* triglycollamate,  $C_6H_{10}O_8NBi$ , and a hydrated double salt,  $C_{12}H_{22}O_{17}N_2Na_3Bi$ , of  $Na$  *Bi* triglycollamate with  $Na_2$  triglycollamate.

P. G. M.

**Crystal structure of  $\beta$ -glycylglycine.**—See A., 1943, I, 54.

**Raman spectra of betaine.**—See A., 1943, I, 50.

**Lysine and ornithine.** H. D. Dakin (*J. Biol. Chem.*, 1943, 146, 237–240).—Varying amounts ( $\sim 5$ – $10\%$  of total present) of lysine (I) and ornithine (II) may be pptd. by alternate use of excess of 15% aq.  $AgNO_3$  and  $N$ - or  $2N$ - $NaOH$ , until a brown ppt. of  $Ag_2O$  appears; the ppt. is decomposed by  $HCl$ . Formation of hydantoins by ring-closure of the  $PhNCO$  derivatives of (I) and (II) with  $HCl$  is accompanied by progressive racemisation; the latter is limited by adding  $EtOH$ , which gives quick dissolution and reaction (2.5 min.). Thus prepared are optically homogeneous hydantoin derivatives of *d*-lysine, m.p.  $200$ – $202^\circ$ ,  $[\alpha]_D^{20} - 62.5^\circ$  in  $C_5H_5N$  (from aq.  $AcOH$ ), and *d*-ornithine, m.p.  $208$ – $209^\circ$ ,  $[\alpha]_D^{20} - 48.0^\circ$  in  $C_5H_5N$ ; derivatives from inactive (I) or (II) melt at  $190$ – $191^\circ$  and  $191$ – $192^\circ$ , respectively. A partly racemised hydantoin can be completely racemised by 0.5*N*- $NaOH$  in 24 hr.

A. T. P.

**Preparation of asparagine.**—See A., 1943, III, 74.

**Action of enzymes on  $\alpha\alpha'$ -iminodicarboxylic acids.** P. Karrer and R. Appenzeller [with, in part, A. Kugler] (*Helv. Chim. Acta*, 1942, 25, 1149–1154; cf. A., 1942, II, 278).—*dl*-Leucine and *dl*- $CHMeBr\cdot CO_2H$  (I) in  $N$ - $NaOH$  at  $37^\circ$  give *r*- $\alpha\alpha'$ -iminopropionic-hexoic acid, m.p.  $239^\circ$ . *l*-Leucine (II) and *l*- $CHMeBr\cdot CO_2H$  afford (+)- $\alpha\alpha'$ -iminopropionic-hexoic acid, m.p.  $214^\circ$ ,  $[\alpha]_D^{18} + 16^\circ$ , whilst  $\alpha\alpha'$ -iminopropionic-*l*-hexoic acid, m.p.  $233^\circ$  (decomp.),  $[\alpha]_D \pm 0^\circ$  in  $H_2O$ , is derived from (II) and *d*- $CHMeBr\cdot CO_2H$ . *dl*- $\alpha\alpha'$ -Imino-aceticpropionic acid, m.p.  $217^\circ$  (decomp.), is derived from (I) and glycine. These acids are not affected by *d*-amino-acid oxidase (III) or by the *l*-amino-acid oxidase and other enzymes present in fresh liver and kidney tissue. The observed oxidative deamination of *dl*-methylalanine by (III) is confirmed (cf. Keilin *et al.*, A., 1936, 241) but this behaviour is not general for *sec.* amines since it is not shown by *N*-butyl-*dl*-alanine.

H. W.

**Behaviour of polyamides on heating.** R. Brill (*J. pr. Chem.*, 1942, [ii], 161, 49–64).—X-Ray diagrams of threads of the condensate (I) of adipic acid and  $(CH_2)_6N_4$ , and of  $\epsilon$ -aminohexoic acid (II), were obtained at various temp. In the case of (I) the symmetry increases with rise of temp., the monoclinic lattice becoming hexagonal. The transformation temp. is  $\sim 161^\circ$ , but there is considerable hysteresis. In the presence of  $H_2O$  vapour, however, the hysteresis is much diminished and the transformation occurs at  $140^\circ$ . The results for (II) show minor differences from those for (I). In agreement with Fuller *et al.* (A., 1941, I, 103), it is found that at high temp. segments of the polyamide mol. execute rotational vibrations. In the case of (I) the orientation achieved mechanically at the beginning of the work is decreased as the temp. rises, whilst for (II) the orientation is increased with rise of temp.

A. J. M.

## II.—SUGARS AND GLUCOSIDES.

**Reactions relating to carbohydrates and polysaccharides.** LXVII. **Synthesis of methylated glucose derivatives.** T. H. Evans, I. Levi, W. L. Hawkins, and H. Hibbert (*Canad. J. Res.*, 1942, 20, B, 175–184).— $\alpha$ -Methylglucoside (from glucose,  $MeOH$ , and  $HCl$ ) with  $PhCHO$  (anhyd.  $ZnCl_2$ ) yields 4:6-benzylidene- $\alpha$ -methylglucoside, new m.p.  $163$ – $164^\circ$ , methylated ( $Me_2SO_4$ - $NaOH$  in  $N_2$ ) and hydrolysed (0.275*N*- $H_2SO_4$  in  $N_2$ ) to 2:3-dimethyl- $\alpha$ -methylglucoside, m.p.  $81.5$ – $83^\circ$ . 2:3-Dimethylgluconophenylhydrazide, from the gluconic acid and  $NHPh\cdot NH_2$  in boiling  $Et_2O$ , has m.p.  $166.5$ – $167^\circ$ . 2:3-Dimethyl- $\beta$ -methylglucoside is prepared either from  $\beta$ -methylglucoside via the 4:6- $CHPh$  derivative, or from 2:3-dimethylglucose via the  $Bz_3$  compound. 2:3:4-Trimethyl-*l*-glucosan on methylation and hydrolysis (as above) yields 2:3:4-trimethylglucose, which with  $MeOH$ - $HCl$  gives 2:3:4-trimethyl- $\alpha$ - and - $\beta$ -methylglucosides, the former methylated (as above) to 2:3:4:6-tetramethyl- $\alpha$ -methylglucoside, hydrolysed (5%  $H_2SO_4$ ) to 2:3:4:6-tetramethylglucose.

A. Li.

**Rates of reaction of diisopropylidene-glucose, -galactose, and -sorbose with *p*-toluenesulphonyl chloride in pyridine solution.** R. C. Hockett and M. L. Downing (*J. Amer. Chem. Soc.*, 1942, 64, 2463–2464).—Reaction of *p*- $C_6H_4Me\cdot SO_2Cl$  (I) (8 mols.) with 1:2:5:6-diisopropylidene-*D*-glucose, 2:3:4:6-diisopropylidene-*L*-sorbose, or 1:2:3:4-diisopropylidene-*D*-galactose (1 mol.) in  $C_5H_5N$  at  $23^\circ$  is found polarimetrically to be pseudounimol. and have half-change times in the ratio 74.2:2.1:1. The selectivity of (I) for primary or *sec.*  $OH$  thus closely resembles that of  $CPh_3Cl$  (cf. A., 1942, II, 6).

R. S. C.

**Agar-agar. III. Isolation of hepta-acetyl-*dl*-galactose from 3:6-anhydro- $\beta$ -methyl-*d*-galactoside.** T. L. Cottrell and E. G. V. Percival. IV. E. G. V. Percival and T. G. H. Thomson (*J.C.S.*, 1942, 749–750, 750–755).—III. 3:6-Anhydro- $\beta$ -methyl-*d*-galactoside with  $Ac_2O$ - $H_2SO_4$  at  $37^\circ$  yields *dl*-galactose hepta-acetate, similarly obtained (Pirie, A., 1936, 593) from agar, which probably therefore contains 3:6-anhydro-*l*-galactose units.

IV. Washed, methylated agar with  $AcBr$  in  $CHCl_3$  yields *Me\_5* methyl-*d*-galactonate (I), m.p.  $46^\circ$ ,  $[\alpha]_D^{14} + 20^\circ$  in  $H_2O$ , and a mixture of methylated disaccharide esters hydrolysed (5%  $H_2SO_4$ ) to 2:5-dimethyl-3:6-anhydro-*l*-galactonic acid, m.p.  $160^\circ$ ,  $[\alpha]_D^{14} - 65^\circ$  in  $H_2O$  (the amide, m.p.  $171^\circ$ , gives a negative Weerman reaction), tetramethyl-*d*-galactopyranose (isolated as anilide), and 2:4:5:6-tetramethyl-*d*-galactonic acid (syrup),  $[\alpha]_D^{14} - 3^\circ$  in  $H_2O$ , the *Me* ester, b.p.  $110$ – $135^\circ/0.07$  mm.,  $[\alpha]_D^{15} + 11^\circ$  in  $H_2O$ , of which with  $MeOH$ - $NH_3$  yields an amide (syrup) giving a negative Weerman reaction, and with  $MeI$  and  $Ag_2O$  gives (I). Hydrolysis ( $MeOH$ - $HCl$ ) of methylated agar gives no tetramethyl-*d*-galactopyranose (cf. A., 1937, II, 445), but the production of dimethylmethylgalactosides is confirmed, and a small amount of substance is formed which when methylated, hydrolysed, and treated with  $NH_2Ph$  yields tetramethyl-*l*-galactoseanilide, m.p.  $197^\circ$ ,  $[\alpha]_D^{20} + 70^\circ$  in  $COMe_2$ . Hydrolysis ( $H_2O$  at  $130^\circ$  under pressure) of agar yields a gel, " $\delta$ ," and a  $H_2O$ -sol. fraction, " $\lambda$ ." These have been acetylated, methylated, and hydrolysed, and the relative mol. wts. of the products determined ( $\eta$  and  $I$  val.), but the results do not explain the differences in properties of " $\delta$ " and " $\lambda$ ."

A. Li.

**Action of diazomethane on acyclic sugar derivatives. III. Synthesis of ketoses and of their open-chain (keto) acetates.** M. L. Wollrom, S. W. Waisbrot, and R. L. Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 2329—2331; cf. A., 1942, II, 395).—1-Diazo-1-deoxyketo-d-fructose tetra-acetate in boiling AcOH gives keto-d-fructose penta-acetate (Hudson *et al.*, A., 1916, i, 116), thus proving the nature of the reaction. 1-Diazo-1-deoxyketo-d-glucoheptulose penta-acetate gives similarly keto-d-glucoheptulose hexa-acetate (70%), m.p. 104—105°,  $[\alpha]_D^{25} + 18.7^\circ$  in  $\text{CHCl}_3$  [absorption max. at 2830 Å. ( $\log \epsilon 1.60$ )], also obtained from 1-bromoketo-d-glucoheptulose penta-acetate by  $\text{KOAc}-\text{Ac}_2\text{O}$  at 70° and converted by  $\text{NH}_3-\text{MeOH}$  at 0° and then  $\text{Ac}_2\text{O}-\text{NaOAc}$  at 100° into the cyclic hexa-acetate, m.p. 114.5—115.5°,  $[\alpha]_D^{25} + 86^\circ$  in  $\text{CHCl}_3$  (cf. lit.). Mucyl dichloride tetra-acetate with  $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O}$  at <0° gives "1:8-bisdiazomucyldimethane" tetra-acetate (A; R =  $\text{CHN}_2$ ), m.p. 179—180° (decomp.), which with  $\text{HCl}-\text{Et}_2\text{O}$  or boiling AcOH gives "1:8-dichloromucyldimethane" tetra-acetate (A; R =  $\text{CH}_2\text{Cl}$ ), m.p. 174—175°, and "1:8-dihydroxymucyldimethane" hexa-acetate (A; R =  $\text{CH}_2\text{OAc}$ ), m.p. 193—195° (decomp.), respectively.

R. S. C.

**Fructosan from *Yucca mohavensis*, Sarg.** K. P. Dimick and B. E. Christensen (*J. Amer. Chem. Soc.*, 1942, **64**, 2501—1502).—The fat-free stem of this plant yields to 70% EtOH 42% of a fructosan (Ba salt; acetate), possibly a fructopyranose and similar to that from rye flour (A., 1935, 69).

R. S. C.

**Optical rotatory power of crocin in true and in colloidal solution.** R. Kuhn and I. Low (*Kolloid.-Z.*, 1942, **100**, 136—137).—The extremely high optical activity shown by crocin in aq. (colloidal) solution (cf. A., 1939, II, 246) becomes negligibly small when the substance is in true solution in MeOH, AcOH,  $\text{C}_5\text{H}_5\text{N}$ , or 10% aq.  $\text{C}_5\text{H}_5\text{N}$ .

F. L. U.

**Structure of the dextrans isolated from maize syrup.** M. Levine, J. F. Foster, and R. M. Hixon (*J. Amer. Chem. Soc.*, 1942, **64**, 2331—2337).—Prep. of dextrans from maize syrup, essentially by MeOH, is described. Fractional pptn. from  $\text{H}_2\text{O}$  by MeOH gives fractions containing 2—26 (average) glucose units, the higher fractions being free from maltose or glucose. I-KOH yields K dextrinates, the K content of which agrees with the mol. wt. calc. from the I-reducing power and with  $[\alpha]$ . Methylation is smoothly effected by Na-Mel in liquid  $\text{NH}_3$ ; determination, after hydrolysis, of tetramethylglucose shows absence of branching (confirmed by absence of dimethylglucose) and non-reducing fractions (confirmed by  $[\alpha]$ ). The smaller dextrans give quantitatively unstable compounds of phenylhydrazide type; the larger dextrans (<6 units) absorb  $\text{NHPH}\cdot\text{NH}_2$ ; a stereochemical explanation is offered.

R. S. C.

**Action of aqueous sodium hydroxide on starch. Strengthening of intramolecular linkings.** C. Dumazert and R. Michel (*Compt. rend.*, 1942, **214**, 645—647; cf. A., 1939, II, 470).—If starch is pretreated with aq. NaOH, degradation by  $\text{H}_2\text{SO}_4-\text{EtOH}$  is arrested and hydrolysis by pancreatic amylase is much slower, thus suggesting a greater stability of certain intramol. linkings.

A. T. P.

**Investigation of the constitution of starch from the action on it of starch-splitting enzymes.** K. Myrbäck (*Tekn. Samfund. Handl.*, 1941, 79—129).—The action of dextrinogen amylase (I) on starch (II) gives ~21% of "limit" dextrin (III) having 6, 4, and, especially, 3 glucose residues per mol. Taka-amylase gives ~20% of (III) (6 residues per mol.), and small quantities of tetra- and tri-saccharides. Pancreatic or salivary amylases, however, produce chiefly tetrasaccharides and ~25 and 27% of (III), respectively, since the enzymes which decompose (III) specifically are absent. If (I) contains no  $\text{PO}_4^{''}$  the whole of the  $\text{P}_2\text{O}_5$  of (II) is to be found in (III), especially in those of high mol. wt.;  $\text{PO}_4^{''}$  has no influence on the rate of decrease of (III) formation. Presence of reducing groups (e.g.,  $\cdot\text{CHO}$ ) in the substrate is (contrary to K. Meyer's theory) without important influence on the saccharoamylase activity.

J. G.

**Starch studies: preparation and properties of starch triesters.** J. W. Mullen and E. Pacsu (*Ind. Eng. Chem.*, 1942, **34**, 1209—1217; cf. B., 1942, III, 214).—Methods for the prep. of starch esters are critically reviewed and a preferred method is described involving gelatinisation of starch in azeotropic  $\text{C}_5\text{H}_5\text{N}-\text{H}_2\text{O}$ , and acylation in presence of  $\text{C}_5\text{H}_5\text{N}$  as catalyst. The triacetates, tripropionates, and tributyrates have been prepared from 5 varieties of starch and their physical properties studied. Special discussion is devoted to the results for  $\eta$ . The acetates from different starches differ mainly in their mol. wt., due to different contents of amylose and amylopectin; the degree of branching is of secondary importance. The behaviour of starch acetate agrees with the assumption that it forms approx. spheroidal mols.

I. A. P.

**Physico-chemical characteristics of glycogen.** W. B. Bridgman (*J. Amer. Chem. Soc.*, 1942, **64**, 2349—2356).—Glycogen, prepared by acid or base, is non-homogeneous. It lies mainly in the range of sedimentation const. 20—120S. The max. ( $S_{20} = 70\text{S}$ ) corresponds to a mol. wt.  $2 \times 10^6$  if the particle is spherical or  $4 \times 10^6$  if frictional resistance is evaluated by the measured diffusion const. c 2 (A., II.)

This mol. wt. may be that of an aggregate or chemical mol. Interpretation of results on non-homogeneous systems is discussed.

R. S. C.

**Determination of the mol. wt. of cellulose by an end-group method.** E. Husemann and O. H. Weber (*J. pr. Chem.*, 1942, [ii], **161**, 1—19).—Practical details of a method already outlined (A., 1943, I, 8) are given.

A. J. M.

**Connexion between carboxyl content and degree of polymerisation of celluloses and the ripening of viscose and its bleaching by chlorine.** O. H. Weber and E. Husemann (*J. pr. Chem.*, 1942, [ii], **161**, 20—29).—The oxidation of cellulose has been investigated by finding the  $\cdot\text{CO}_2\text{H}$  content by the reversible methylene-blue method, and the  $\eta$  in Schweitzer's reagent, and calculation from the latter of the degree of polymerisation by Staudinger's method. Under the action of atm.  $\text{O}_2$  on Na-cellulose, a splitting of the cellulose chain takes place with formation of 1  $\text{CO}_2\text{H}$  for each broken linking. The effect of  $\text{Cl}_2$  on cellulose in the bleaching process is investigated for solutions of different pH. From comparison of degrees of polymerisation and monose nos. it is clear that in acid solutions (pH 0.9) there is considerable breakdown of the mol. In addition to monocarboxylic acids, mols. containing no  $\text{CO}_2\text{H}$  are formed. At pH 5.5, the breakdown does not proceed so far and is oxidative. On the alkaline side autoxidation occurs.

A. J. M.

### III.—HOMOCYCLIC.

**isoButylcyclobutane and dicyclobutylmethane.** B. A. Kazanski and V. P. Golmov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **34**, 196—198).—Passage of cyclobutanecarboxylic acid (I) and  $\text{Pr}^{\beta}\text{CO}_2\text{H}$  over  $\text{ZnO}-\text{MnO}$  at 400—403° gives isobutyron, cyclobutyl  $\text{Pr}^{\beta}$  ketone (II), b.p. 162—164° (yield 37%), and dicyclobutyl ketone (III), b.p. 201°/731 mm., 104°/30 mm. (semicarbazone, m.p. 129—130°), better obtained under identical conditions from (I) alone. (II) gives semicarbazones, prisms, m.p. 137—138°, and needles, m.p. 114—115°, and with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  affords the hydrazone (IV), b.p. 89—90°/6 mm., and mainly the azine, b.p. 140—141°/6 mm. isoButylcyclobutane, b.p. 119—119.5°/743 mm., is prepared by distillation of (IV) with solid KOH and Pt-C. (III) and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  give the corresponding azine, b.p. 187—188°/7 mm., and (mainly) the hydrazone, b.p. 117—118°/25 mm., converted as above into dicyclobutylmethane, b.p. 160.8—161°/743 mm.

H. W.

**Structure of "diphenylene."** W. Baker (*Nature*, 1942, **150**, 210—211).—"Diphenylene,"  $\text{C}_{12}\text{H}_8$ , prepared by Lothrop's method (A., 1941, II, 247) does not readily yield  $\text{Ph}_2$  on hydrogenation, neither does it show the properties of an acetylene or an allene. The annexed formula is proposed.

A. A. E.

**Structure of "diphenylene."** C. A. Coulson (*Nature*, 1942, **150**, 577—578).—Baker's cyclopentindene formula for the compound  $\text{C}_{12}\text{H}_8$  (see above) is supported by the fact that the bond strain energy is only a few kg.-cal., whilst that in the diphenyl formula is large, possibly ~100 kg.-cal., although the mobile electrons in the latter are more stable than those in the former.

A. A. E.

**New type of aromatic hydrocarbon. Acephenalane and its derivatives.** Buu-Hoi and P. Cagniant (*Compt. rend.*, 1942, **214**, 493—495).—5-Bromoacenaphthene is converted by successive treatments with Mg in presence of EtBr and  $(\text{CH}_2)_2\text{O}$  into  $\beta$ -5-acenaphthylethyl alcohol, b.p. 180°/0.9 mm. (phenylurethane, m.p. 161°), transformed successively through the corresponding bromide (I), b.p. 171°/0.8 mm., m.p. 75°, and nitrile, m.p. 83°, into  $\beta$ -5-acenaphthylpropionic acid, m.p. 189° [corresponding chloride (II), m.p. 104°, and amide, m.p. 149°]. (I) and  $\text{CHNa}(\text{CO}_2\text{Et})_2$  afford  $\text{Et}_2\beta$ -5-acenaphthylethylmalonate, b.p. 220—230°/1.3 mm., hydrolysed and decarboxylated to  $\gamma$ -5-acenaphthylbutyric acid, m.p. 148° (amide, m.p. 182°).  $\text{AlCl}_3$  and (II) in  $\text{PhNO}_2$  at room temp. give 7-ketoacephenalane, m.p. 194° (oxime, m.p. 240°; semicarbazone, decomp. 235—245°), which is reduced (Clemmensen) to acephenalane (III), b.p. 168—170°/1.3 mm., m.p. 122° [additive compound, m.p. 116°, with 1:3:5- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ ]. 7-Ketoacephenalene forms yellow needles, m.p. 177—178°.

H. W.

**Chaulmoogryl quaternary salts.** R. Baltzly, W. S. Ide, and J. S. Buck (*J. Amer. Chem. Soc.*, 1942, **64**, 2514—2515).—Chaulmoogryl bromide and 33%  $\text{NHMe}_2-\text{MeOH}$  at 105—110° give chaulmoogryl-dimethylamine, m.p. >0°, b.p. 170°/0.5 mm. [methiodide, m.p. >170° (decomp.); benzyliodide, dimorphic, m.p. 99°]. Trimethyl-, mp. 227—230° (decomp.), and benzyldimethyl-octadecylammonium iodide, m.p. 93°, are also described.

R. S. C.

cycloHexylsulphamic acid.—See B., 1943, II, 44.

**p-Aminodimethylaniline. II. o-Chloro- and -nitro-derivatives.** E. E. Ayling, J. H. Gorvin, and L. E. Hinkel (*J.C.S.*, 1942, 755—758; cf. A., 1941, II, 359).—p- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$  (I) affords (method: Pinnow *et al.*, A., 1894, i, 281) 1:2:4- $\text{NMe}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{NHAc}$  (90%) (II), m.p. 132° and 122—123 (dimorphs), and N-nitroso-4-acetamidomethylaniline (6%), m.p. 146° (cf. Hodgson *et al.*, A., 1934, 884).

$p$ -NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub> and HNO<sub>3</sub> ( $d$  1.5; 2 mols.) in AcOH-H<sub>2</sub>SO<sub>4</sub> at 0° give 2 : 6 : 4 : 1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(NH<sub>2</sub>)·NMe<sub>2</sub>. NMe<sub>2</sub>Ph-HNO<sub>3</sub>-AcOH and a little NaNO<sub>2</sub> at <15° afford 2 : 4 : 1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·NMe<sub>2</sub>, reduced by SnCl<sub>2</sub> in EtOH-HCl to 2 : 4 : 1-NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)·NMe<sub>2</sub> (III), m.p. 63° (*Ac*, m.p. 163°, and *CHPh* derivative, m.p. 128°). (I) and Cl<sub>2</sub>-CHCl<sub>3</sub> at room temp. yield 2-chloro-4-acetamidodimethylaniline (IV), m.p. 119—120°, also obtained from (II)-Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>-aq. EtOH, followed by diazotisation and treatment with Cu<sub>2</sub>Cl<sub>2</sub>. Diazotised (III) with Cu-bronze, boiling MeOH, or HNO<sub>3</sub>-Cu-bronze or -Cu<sub>2</sub>O, gives  $p$ -NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub> (V). 4 : 2 : 1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Cl·NMe<sub>2</sub>, m.p. 78° [from (V) and Cl<sub>2</sub>-CHCl<sub>3</sub> or from (III) by the diazo-reaction], is reduced by SnCl<sub>2</sub>-HCl to 2-chloro-4-aminodimethylaniline, m.p. 61.5—63° (*stannichloride*), also obtained by hydrolysis (conc. HCl) of (IV). (II) and HNO<sub>3</sub> ( $d$  1.42) in AcOH afford 4 : 2 : 6 : 1-NHAc·C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>·NMe·NO or in HCl-NHAc·C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>·NMe<sub>2</sub>. (IV) in AcOH or HCl similarly gives 2-chloro-6-nitro-N-nitroso-4-acetamidodimethylaniline (VI), m.p. 132—133°, or 2-chloro-6-nitro-4-acetamidodimethylaniline (VII), m.p. 165—166° (attempted hydrolysis causes decomp.), respectively. (VI) is oxidised by HNO<sub>3</sub> ( $d$  1.5) at 0°, then at room temp., to 2-chloro-6 : N-dinitro-4-acetamidomethylaniline (VIII), m.p. 152—153°. (II) or (IV) and Cl<sub>2</sub>-CHCl<sub>3</sub> yield (VII) or 2 : 6-dichloro-4-acetamidodimethylaniline (IX), m.p. 153—154° (*amine*, m.p. 90—91°), respectively. (VII) and aq. Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>-EtOH give the 6-NH<sub>2</sub>-compound, m.p. 152°, converted (diazo-reaction) into (IX). Boiling PhOH and (VI) or (VIII) give 2-chloro-6-nitro-4-acetamidomethylaniline, m.p. 208—209°, also obtained from (VII) and Br-CHCl<sub>3</sub>. 4 : 2 : 6 : 1-NHAc·C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>·NMe<sub>2</sub> and Br-CHCl<sub>3</sub> give 4 : 2 : 6 : 1-NHAc·C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>·NHMe. A. T. P.

**Preparation of symmetrical azo-compounds, the positional influence of the nitro-group on the decomposition of nitronaphthalenediazonium sulphates by cuprous hydroxide, and an improved method for the production of 2-nitronaphthalene.** H. H. Hodgson, E. Leigh, and G. Turner (*J.C.S.*, 1942, 744—746; cf. A., 1942, II, 52). Decomp. of ArN<sub>2</sub>HSO<sub>4</sub> (I) with CuOH at room temp. depends on the positivity of the C to which N<sub>2</sub> is attached. When this is very great, as in 2 : 1-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·N<sub>2</sub>HSO<sub>4</sub>, ArH results, and 85% of 2-C<sub>10</sub>H<sub>7</sub>·NO<sub>2</sub> is obtained. Gradations in positivity are shown in the decomp. of NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·N<sub>2</sub>HSO<sub>4</sub>, with variations of the predominating product, viz., (NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·N)<sub>2</sub> or (NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>)<sub>2</sub>, indicating min. or medium positivity, respectively. The respective % yields of (NAr)<sub>2</sub>, ArOH, and ArH obtained from various (I) and CuOH are quoted in parentheses: Ar = Ph (33; 26.5; 27.5); *o*- (80; trace; trace), *m*- (0; 28; trace; +35% of 3 : 3'-dichlorodiphenyl), and  $p$ -C<sub>6</sub>H<sub>4</sub>Cl (70; 31; trace); *o*- (35; trace; 39.5), *m*- (mainly 3 : 3'-dinitro-azobenzene + -diphenyl; 13% of PhNO<sub>2</sub>), and  $p$ -NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub> (35; 13; 8);  $\beta$ -C<sub>10</sub>H<sub>7</sub> (54; trace; 34); 2 : 1- (65; trace; 25), 1 : 2- (87.5; trace; trace) and 4 : 1-C<sub>10</sub>H<sub>6</sub>Cl (78.3; trace; trace); 1 : 2- (0; trace; 10; +1 : 1'-dinitro-2 : 2'-dinaphthyl), 4 : 1- (trace; 32.5; 31), and 5 : 1-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub> (40.5; 15; 42). Mechanisms of reaction are discussed. 2 : 2'-Dichloro-1 : 1', m.p. 173—174°, and 1 : 1'-dichloro-2 : 2'-azonaphthalene, m.p. 170—171°, are prepared from C<sub>10</sub>H<sub>6</sub>Cl·N<sub>2</sub>Cl, NaOAc, and aq. Na<sub>2</sub>SO<sub>3</sub> at room temp., then at 60°. 5 : 5'-Dinitro-1 : 1'-azonaphthalene (I), m.p. 322—323°, is obtained similarly. 5 : 1-C<sub>10</sub>H<sub>6</sub>I·NO<sub>2</sub> and Cu-bronze at 220—230° yield 5 : 5'-dinitro-1 : 1'-dinaphthyl, m.p. 228—229°. 5 : 1-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·N<sub>2</sub>HSO<sub>4</sub> and Cu paste or Cu-bronze give 1-C<sub>10</sub>H<sub>7</sub>·NO<sub>2</sub>, 5 : 1-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·OH (trace), and (I) (mainly); Cu-bronze in EtOH affords 1-C<sub>10</sub>H<sub>7</sub>·NO<sub>2</sub>. A. T. P.

**Action of cuprous oxide on diazotised amines in ethyl-alcoholic acid solution.** H. H. Hodgson and H. S. Turner (*J.C.S.*, 1942, 748—749).—NH<sub>2</sub>Ar are efficiently deaminated when ArN<sub>2</sub>HSO<sub>4</sub> (prep. by NO·SO<sub>4</sub>H-AcOH) are added to finely divided Cu<sub>2</sub>O in EtOH; % yields of ArH are: Ar =  $p$ -C<sub>6</sub>H<sub>4</sub>Me (45); *o*- (89), *m*- (78), and  $p$ -NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub> (97); *o*-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub> (65); 2 : 5 : 1-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub> (57); 3 : 5 : 1 : 4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Me (40); (C<sub>6</sub>H<sub>4</sub>-*p*)<sub>2</sub> (49);  $\beta$ -C<sub>10</sub>H<sub>7</sub> (60); 1 : 2- (70) and 2 : 1-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub> (79); 2 : 4 : 1-NO<sub>2</sub>·C<sub>10</sub>H<sub>5</sub>Cl (94); 4 : 2 : 1-NO<sub>2</sub>·C<sub>10</sub>H<sub>5</sub>I (80); 2 : 4 : 1-(NO<sub>2</sub>)<sub>2</sub>C<sub>10</sub>H<sub>5</sub> (65); 1- (75) and 2-anthraquinonyl (70%). A. T. P.

**Influence of  $p$ -substituents on the decomposition of zinc chloride double salts of diazonium chlorides by acetic anhydride.** H. H. Hodgson and C. K. Foster (*J.C.S.*, 1942, 747—748; cf. A., 1942, II, 401).—( $p$ -C<sub>6</sub>H<sub>4</sub>R·N<sub>2</sub>)<sub>2</sub>ZnCl<sub>2</sub> (I) with hot Ac<sub>2</sub>O gives (mainly)  $p$ -C<sub>6</sub>H<sub>4</sub>R·OAc (II) and  $p$ -C<sub>6</sub>H<sub>4</sub>RCl. The comparative influence of R towards OAc replacement is in the decreasing order of the negative ( $-I$ ) effect, viz., Cl > OMe > Me; OH is anomalous. ( $\beta$ -C<sub>10</sub>H<sub>7</sub>·N<sub>2</sub>Cl)<sub>2</sub>ZnCl<sub>2</sub> and Ac<sub>2</sub>O at 60—95° give  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OAc (48%; part hydrolysed to  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH) and 2-C<sub>10</sub>H<sub>7</sub>Cl (23.5%); (I) (R = OH) (at ~110°) yields  $p$ -C<sub>6</sub>H<sub>4</sub>(OAc)<sub>2</sub> (70%) and  $p$ -C<sub>6</sub>H<sub>4</sub>Cl·OH (18.8%). (II) (R = Cl, Me, and OMe) are determined as  $p$ -C<sub>6</sub>H<sub>4</sub>R·OH (49, 38.6%) and  $p$ -C<sub>6</sub>H<sub>4</sub>R·OMe (39%), respectively. A. T. P.

**Mutual influence of chromophoric groups in systems with closed  $\pi$  electron groups.**—See A., 1943, I, 49.

**C-Alkylation of phenols.**—See B., 1943, II, 43.

**Bromination of 4-diphenyl chloroacetate.** S. E. Hazlet, L. C. Hensley, and H. Jass (*J. Amer. Chem. Soc.*, 1942, 64, 2449—2450).—4-Diphenyl chloroacetate (prep. by CH<sub>2</sub>Cl·COCl-C<sub>5</sub>H<sub>5</sub>N-dioxan),

m.p. 116—117°, b.p. 185°/3 mm., with Br and a trace of Fe powder in CCl<sub>4</sub> at 70—80° gives 26% or in CH<sub>2</sub>Cl·CHCl<sub>2</sub> gives 60% of 4'-bromo-4-diphenyl chloroacetate, m.p. 141—142.8° (also obtained from  $p$ -C<sub>6</sub>H<sub>4</sub>Br·C<sub>6</sub>H<sub>4</sub>·OH-*p* and hydrolysed thereinto), but in AcOH gives, according to the grade of AcOH and conditions,  $p$ -C<sub>6</sub>H<sub>4</sub>Ph·OH + 4 : 2 : 6 : 1 C<sub>6</sub>H<sub>2</sub>PhBr<sub>2</sub>·OH, CH<sub>2</sub>Cl·CO<sub>2</sub>H +  $p$ -C<sub>6</sub>H<sub>4</sub>Ph·OAc, or 4-diphenyl bromoacetate, b.p. 185°/3 mm., m.p. 112—112.5°. 2-Bromo- and 2 : 6-dibromo-4-diphenyl chloroacetate have m.p. 60.5—62° and 83—84°, respectively. R. S. C.

**Esters of sec.-hydroxyaralkylalkylamines.** J. S. Buck and R. Baltzly (*J. Amer. Chem. Soc.*, 1942, 64, 2263—2264).— $p$ -OMe·C<sub>6</sub>H<sub>4</sub>·[CH<sub>2</sub>]<sub>2</sub>·NH·CH<sub>2</sub>Ph with CH<sub>2</sub>O (1.1 mol.) and HCO<sub>2</sub>H (5 mols.) etc. gives benzyl- $\beta$ -*p*-anisylethylmethylamine hydrochloride (I), m.p. 170°, but the 3 : 4-(OMe)<sub>2</sub>-compound was not thus methylated. With conc. HCl-CO<sub>2</sub> at 170°, (I) gives benzyl- $\beta$ -*p*-hydroxyphenylethylmethylamine hydrochloride, m.p. 198° [O-acetate, m.p. 211°, -benzoate, m.p. 191°, and -CO<sub>2</sub>Et-derivative (prep. by ClCO<sub>2</sub>Et-NaOH-N<sub>2</sub>), m.p. 128—129°, hydrochlorides]. Hydrogenation (Pd-C) of the appropriate salts in 80% AcOH gives PhMe and  $\beta$ -*p*-acetoxyl-, m.p. 194°,  $\beta$ -*p*-benzoyloxy-, m.p. 198°, and  $\beta$ -*p*-carbethoxyoxyphenylethylmethylamine hydrochloride, m.p. 138.5—139°. 3 : 4 : 1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·[CH<sub>2</sub>]<sub>2</sub>·NHMe and CH<sub>2</sub>PhCl-EtOH at room temp. give benzyl- $\beta$ -homoveratrylmethylamine hydrochloride (30%), m.p. 205°, and thence, as above, benzyl- $\beta$ -3 : 4-dihydroxy-, m.p. 153° (diacetate, m.p. 174—175°; dibenzoate, m.p. 131—132°), and  $\beta$ -3 : 4-diacetoxyl-, m.p. 142—143°, -dibenzoyloxy-, m.p. 163—164°, and -di(carbethoxyoxy)-, m.p. 115°, -phenylethylmethylamine hydrochloride. R. S. C.

**Mixed aromatic phosphates.**—See B., 1943, II, 44.

**Use of deuterium as a tracer in the Claisen rearrangement.** G. B. Kistiakowsky and R. L. Tichenor (*J. Amer. Chem. Soc.*, 1942, 64, 2302—2304).—When nuclear-deuterated Ph allyl ethers rearrange, the D displaced migrates entirely to the O. 2 : 4 : 6 : 1-C<sub>6</sub>H<sub>2</sub>D<sub>3</sub>·OH and 4 : 2 : 6 : 1-C<sub>6</sub>H<sub>2</sub>DMe<sub>2</sub>·OH, prepared from the phenol by D<sub>2</sub>O-HCl at 100°, with CH<sub>2</sub>:CH·CH<sub>2</sub>Br-NaOH-H<sub>2</sub>O-COMe<sub>2</sub> at the b.p. give the allyl ethers, which are rearranged at 230—240° and 190—200°, respectively. The products are treated with AcCl, and the DCl-HCl mixture evolved is collected in HCl and analysed for D by infra-red absorption. Migration of D does not occur when 2 : 4 : 6 : 1-CH<sub>2</sub>:CH·CH<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>D<sub>3</sub>·OH is heated at 210—230°. 2 : 6-Dimethyl-4-allylphenol, m.p. 26—27° (phenylurethane, m.p. 137—139°), gives an acetate, b.p. 105—110°/2 mm. R. S. C.

**$\alpha$ -Bromo- $\alpha\beta$ -tri-*p*-anisylethylene [synthetic oestrogenic agent].**—See B., 1943, III, 41.

**Nuclear alkylation of alkylaminophenols.**—See B., 1943, II, 43.

**Synthesis of  $p$ -hydroxyphenyl amyl sulphide.** E. Miller, F. S. Crossley, and M. L. Moore (*J. Amer. Chem. Soc.*, 1942, 64, 2322—2323).— $p$ -OH·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Cl and *n*-C<sub>5</sub>H<sub>11</sub>·SH (I) in aq. NaOH at 10° and then 60° give  $p$ -OH·C<sub>6</sub>H<sub>4</sub>·S·C<sub>5</sub>H<sub>11</sub>-*n* (25—30%), m.p. 62—62.5°, and (*n*-C<sub>5</sub>H<sub>11</sub>·S)<sub>2</sub>, b.p. 89—91°/1 mm., reduced by Na-EtOH to (I) and obtained also from *n*-C<sub>5</sub>H<sub>11</sub>Br by Na<sub>2</sub>S<sub>2</sub>-EtOH or from (I) by I-NaOH-H<sub>2</sub>O.  $p$ -OH·C<sub>6</sub>H<sub>4</sub>·S·C<sub>5</sub>H<sub>11</sub>-*iso* is similarly prepared. R. S. C.

**Polyene series. V. Employment of  $\gamma$ -2 : 6 : 6-trimethyl- $\Delta^1$ -cyclohexenyl- $\alpha$ -methylcrotonaldehyde for the synthesis of vitamin-A and analogues.** I. M. Heilbron, A. W. Johnson, E. R. H. Jones, and A. Spinks (*J.C.S.*, 1942, 727—733; cf. A., 1939, II, 548).—The synthesis of vitamin-A described by Kuhn *et al.* (A., 1937, II, 288) could not be repeated. NaOMe (added slowly),  $\beta$ -ionone, b.p. 82°/10<sup>-2</sup> mm. (regenerated from the semicarbazone), and CH<sub>2</sub>Cl·CO<sub>2</sub>Et in light petroleum (b.p. 40—60°) in N<sub>2</sub> first at -60°, then at 20° (18 hr.), and finally at the b.p. (6 hr.), give *Et*  $\alpha\beta$ -oxido- $\delta$ -2 : 6 : 6-trimethyl- $\Delta^1$ -cyclohexenyl- $\beta$ -methyl- $\Delta^2$ -pentenoate, b.p. 55° (bath)/10<sup>-3</sup> mm., hydrolysed (10% KOH-EtOH at 20°; then 4N-H<sub>3</sub>PO<sub>4</sub>) to the corresponding acid (I), m.p. 132° (decomp.) (poor yield) [Me ester, b.p. 70—80° (bath)/10<sup>-4</sup> mm.], stable only in N<sub>2</sub> in the dark. There is no evidence that (I) or its esters exist in the isomeric CO-form. There is a marked difference in the intensities of absorption at 2860 Å. between the Et ester and (I) or its Me ester, and a variation in  $\eta$  is noted in the case of the esters; similar variations occur with the esters (below) from mesityl oxide, and are ascribed to the existence of stereoisomeric forms of the glycidic acid.  $\alpha$ -Ionone, (reaction in Et<sub>2</sub>O) similarly affords *Et*  $\alpha\beta$ -oxido- $\delta$ -2 : 6 : 6-trimethyl- $\Delta^2$ -cyclohexenyl- $\beta$ -methyl- $\Delta^2$ -pentenoate, b.p. 135—145°/0.2 mm., 70° (bath)/10<sup>-4</sup> mm.; the derived acid (II) did not crystallise. Mesityl oxide and CH<sub>2</sub>Cl·CO<sub>2</sub>Et-NaOMe-Et<sub>2</sub>O give a mixture of *Et*, b.p. 65°/1 mm., and *Me*  $\alpha\beta$ -oxido- $\beta\delta$ -dimethyl- $\Delta^2$ -hexenoate, b.p. 60°/1 mm., hydrolysed to the acid (III), m.p. 72°. The oxido-group in the above esters largely resembles an ethylenic linking in absorption properties. Crude (I) and Cu at 130°/15 mm. (1.5 hr.) afford a non-ketonic fraction, b.p. 80—90°/0.1 mm., and  $\gamma$ -2 : 6 : 6-trimethyl- $\Delta^1$ -cyclohexenyl- $\alpha$ -methylcrotonaldehyde (IV), b.p. 45° (bath)/10<sup>-4</sup> mm. (phenylsemicarbazone, m.p. 182°; 2 : 4-dinitrophenylhydrazones, m.p. 164.5°), purified by regeneration from the thiosemicarbazone, m.p. 192°, by steam-distillation in presence of *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O in N<sub>2</sub>. The  $\alpha\beta$ -unsaturated nature is shown by its absorption spectrum (cf. Ishikawa *et al.*, A., 1937, II, 426). (II) is decarboxylated

similarly 1:  $\gamma$ -2: 6: 6-trimethyl- $\Delta^2$ -cyclohexenyl- $\alpha$ -methylcrotonaldehyde, b.p. 45 (bath)/10<sup>-4</sup> mm. (regenerated from the thiosemicarbazone, m.p. 138—150°; phenylsemicarbazone, m.p. 123—124°; 2: 4-dinitrophenylhydrazones, m.p. 148.5—149.5°), with light absorption data analogous to those of (IV). The two aldehydes described by Ishikawa *et al.* (*loc. cit.*) are probably identical, being derived from  $\alpha$ -ionone. (III) and Cu at 145°/760 mm. give a mixture, b.p. 125—135°, which affords, through the semicarbazone, m.p. 184°, (mainly)  $\alpha$ -dimethyl- $\Delta^2$ -pentenaldehyde, CHPh $\beta$ :CMe:CHO, b.p. 130—135° (phenylsemicarbazone, m.p. 178°; 2: 4-dinitrophenylhydrazones, m.p. 164—165°). (IV), COMe<sub>2</sub>, and Al(Obu<sup>n</sup>)<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> and N<sub>2</sub> give  $\eta$ -2: 6: 6-trimethyl- $\Delta^1$ -cyclohexenyl- $\varepsilon$ -methyl- $\Delta^{10}$ -heptadien- $\beta$ -one, b.p. 75—80° (bath)/10<sup>-4</sup> mm. [semicarbazone, m.p. 189—190° (decomp.)], converted by MgEtBr into  $\theta$ -2: 6: 6-trimethyl- $\Delta^1$ -cyclohexenyl- $\gamma$ - $\zeta$ -dimethyl- $\Delta^8$ -octadien- $\gamma$ -ol, b.p. 70—80° (bath)/10<sup>-4</sup> mm. CH<sub>2</sub>:CNa [from C<sub>2</sub>H<sub>2</sub> and Na (not NaNH<sub>2</sub>) in liquid NH<sub>3</sub>] and citral in Et<sub>2</sub>O give  $\alpha$ -acetylenylgeraniol (V), CMe<sub>2</sub>:CH·[CH<sub>2</sub>]<sub>2</sub>:CMe:CH·CH(OH)·C $\beta$ :CH, b.p. 88°/0.02 mm., which with Ac<sub>2</sub>O·C<sub>5</sub>H<sub>5</sub>N at 100° in N<sub>2</sub> affords the acetate, b.p. 92—95°/0.5 mm. (absorption spectrum similar to that of the carbinol); prolonged treatment of (V) with Ac<sub>2</sub>O at 110° gives (mainly)  $\varepsilon$ -dimethyldeca- $\Delta^{10}$ -triene- $\Delta^1$ -inene. (IV) similarly yields  $\zeta$ -2: 6: 6-trimethyl- $\Delta^1$ -cyclohexenyl- $\delta$ -methylhex- $\Delta^8$ -ene- $\Delta^1$ -inene- $\gamma$ -ol, b.p. 115—120°/10<sup>-3</sup> mm.; the acetate, b.p. 130—135°/0.1 mm., shows light absorption data indicating some migration of a double linking. A. T. P.

**Polyene series. VI. Preparation of ethynylcarbinols from  $\alpha\beta$ -unsaturated aldehydes. VII. Carbinols from propargyl acetal.**—See A., 1943, II, 53, 54.

**Physiologically active phenylethylamines containing a *tert.* hydroxyl.** C. M. Suter and A. W. Weston (*J. Amer. Chem. Soc.*, 1942, **64**, 2451—2452).—The appropriate Grignard reagent and CPh·CHR·NHR',HCl give  $\beta$ -hydroxy- $\beta$ -phenyl-*n*-butyl-, m.p. 180—181° (lit. 183.5°, 184—186°), and -*n*-hexyl-amine hydrochloride, m.p. 151—152°,  $\beta$ -amino- $\gamma$ -phenyl-*n*-butan-, m.p. 239—239.5° (decomp.) (lit. 244°), -*n*-pentan-, m.p. 220.5—222° (decomp.), -*n*-heptan-, m.p. 213—216° (decomp.), and -*n*-nonan-, m.p. 193—200° (decomp.), - $\gamma$ -ol hydrochloride,  $\beta$ -amino- $\alpha$ -cyclohexyl- $\alpha$ -phenylpropan- $\alpha$ -ol hydrochloride, +2H<sub>2</sub>O, m.p. 261—263° (decomp.),  $\beta$ -methylamino- $\gamma$ -phenyl-*n*-butan-, m.p. 234—235° (lit. 245—248°), -*n*-pentan-, m.p. 197.5—198.5° (decomp.) (lit. 192°), -*n*-hexan-, m.p. 182.5—183.5° (decomp.), -*n*-heptan-, m.p. 149—150°, and - $\Delta^6$ -*n*-hexen-, m.p. 166.5—167.8°, - $\gamma$ -ol hydrochloride. M.p. are corr. Alk in the grouping CAlk·C·NH has little effect on the pressor activity but reduces the toxicity. Some of the products are irritant (rabbits' cornea). R. S. C.

**Hexamethylene O-acylmandelates.**—See B., 1943, III, 41.

**Preparation of phenylpropionic acid.** M. Reimer (*J. Amer. Chem. Soc.*, 1942, **64**, 2510).—Prep. of CPh $\beta$ :C·CO<sub>2</sub>H from CHPh $\beta$ :CH·CO<sub>2</sub>H by way of the dibromide (prep. in boiling CCl<sub>4</sub>) is improved to 76% over-all yield. R. S. C.

**Nitration of 4-diphenyl benzoate.** S. E. Hazlet and H. O. Van Orden (*J. Amer. Chem. Soc.*, 1942, **64**, 2505—2506).—*p*-C<sub>6</sub>H<sub>4</sub>Ph·OBz with fuming + conc. HNO<sub>3</sub> in AcOH at room temp. gives 4'-nitro-4-diphenyl benzoate, m.p. 209—210°, also obtained from *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·C<sub>6</sub>H<sub>4</sub>·OH-*p*. 2-Nitro-, m.p. 111°, 2: 6-, m.p. 157—158°, and 2: 4'-dinitro-, m.p. 151—152°, and 2: 6: 4'-trinitro-4-diphenyl benzoate, m.p. 168°, are described. R. S. C.

**Chemical constitution and the tanning effect. I. Simple esters and polyesters of gallic acid.** A. Russell and W. G. Tebbens, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2274—2276).—Gallic acid and ROH·HCl give *n*-amyl (I), m.p. 127°, and *n*-hexyl gallate (II), m.p. 92°. 3: 4: 5: 1-(OAc)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>·COCl and *d*-arabitol in quinoline·CHCl<sub>3</sub> at room temp. give *d*-arabityl pentatriacetylgallate, m.p. 72° after sintering, hydrolysed by NaOH·H<sub>2</sub>O·COMe<sub>2</sub>·N<sub>2</sub> at 0° to *d*-arabityl pentagallate (III), m.p. 83° after sintering. Relative tanning properties are: very good, gallotannin; fair, (III), *dl*-erithrityl tetragallate, mannityl and sorbitol hexagallate, m.p. 76° after sintering; poor, ethylene glycol di- and glyceryl tri-gallate; none, gallic acid, Me, Et, Pr <sup>$\alpha$</sup> , Pr <sup>$\beta$</sup> , and Bu <sup>$\alpha$</sup>  gallate, (I), (II). (CH<sub>2</sub>·OH)<sub>2</sub>, glycerol, *dl*-erythritol, *d*-arabitol, sorbitol. R. S. C.

**Condensation of phenylglyoxylic acid with phenylacetonitrile.** M. Cordier and J. Moreau (*Compt. rend.*, 1942, **214**, 621—623; cf. A., 1935, 975).—CPh·CO<sub>2</sub>H and CH<sub>2</sub>Ph·CN condense with difficulty in presence of aq. alcoholic alkali, but in piperidine (~2 mols.) alone,  $\alpha$ -hydroxy- $\beta$ -cyano- $\alpha\beta$ -diphenylpropionic acid, decomp. slowly >180° or more rapidly ~210°, is obtained (40% yield). It is converted by HCl·AcOH at 100° into (CPh·CO)<sub>2</sub>O. A. T. P.

**Symmetrical cyanostilbenes.** J. B. Niederland and A. Ziering (*J. Amer. Chem. Soc.*, 1942, **64**, 2486—2487).—CH<sub>2</sub>Ar·CN with I·NaOMe·MeOH·Et<sub>2</sub>O gives ~35% of  $\alpha\beta$ -dicyano-4: 4'-dimethoxy-, m.p. 187°-3: 4: 3': 4'-dimethylenedioxy-, m.p. 235°, and -tetramethoxy-stilbene, m.p. 205°. 4: 4'-Dihydroxy- $\alpha\beta$ -dicyanostilbene, m.p. 287° (diacetate, m.p. 217°), obtained (diazo-method) from the (NH<sub>2</sub>)<sub>2</sub>-derivative shows some oestrogenic activity. CHArEt·CN with I·NaNH<sub>2</sub> in Et<sub>2</sub>O gives ~25% of  $\gamma\delta$ -dicyano- $\gamma\delta$ -diphenyl-, m.p. 175°, and -di-3: 4-methylenedioxyphenyl-*n*-hexane, m.p. 213°. *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHEt·CN

(prep. from CHPhEt·CN by fuming HNO<sub>3</sub> at 0°), b.p. 165°/3 mm., with I·NaOMe gives  $\gamma\delta$ -dicyano- $\gamma\delta$ -di-*p*-nitro-, m.p. 225°, and thence -*p*-amino-, m.p. 205°, and -*p*-hydroxy-, m.p. 218°, -phenyl-*n*-hexane. Reactions, CH<sub>2</sub>R·CN (R = 3: 4-CH<sub>2</sub>O<sub>2</sub>:C<sub>6</sub>H<sub>3</sub>) + Et<sub>2</sub>CO<sub>2</sub>·Na·C<sub>6</sub>H<sub>5</sub> (60°) → CN·CHR·CO<sub>2</sub>Et, b.p. 161°/3 mm. → (+EtI·NaOEt·EtOH) → CN·CETR·CO<sub>2</sub>Et, m.p. 72° → (cold alkali) CN·CETR·CO<sub>2</sub>H, m.p. 110° → (180°) CHEtR·CN, b.p. 174°/5 mm., are reported.

R. S. C.

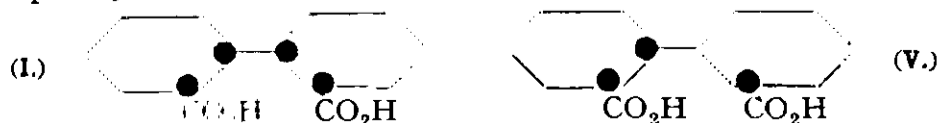
**Acrylonitrile. I. Cyanoethylation of active methylene groups.** H. A. Bruson (*J. Amer. Chem. Soc.*, 1942, **64**, 2457—2461).—In presence of strong bases, CH<sub>2</sub>:CH·CN (I) adds to reactive >CH<sub>2</sub>, giving >CH·[CH<sub>2</sub>]<sub>2</sub>·CN and then >C([CH<sub>2</sub>]<sub>2</sub>·CN)<sub>2</sub>. 40% aq. CH<sub>2</sub>Ph·NMe<sub>3</sub>·OH (II) is an excellent catalyst; solvents (dioxan, Bu <sup>$\gamma$</sup> OH) and cooling are advisable to control the reaction. Fluorene thus affords 9: 9-di- $\beta$ -cyanoethylfluorene (74%), m.p. 121°. Indene gives 1: 1-di-, b.p. 210—220°/2 mm., and much 1: 1: 3-tri- $\beta$ -cyanoethylindene, m.p. 65°, b.p. 280—290°/1 mm. Anthrone gives 9: 9-di- $\beta$ -cyanoethylanthr-10-one, m.p. 215°. 2-Nitrofluorene gives 2-nitro-9: 9-di- $\beta$ -cyanoethylfluorene (~100%), m.p. 236—237°. In absence of a base, cyclopentadiene (III) and (I) give (Diels-Alder) exothermally 2: 5-endomethylene- $\Delta^3$ -tetrahydrobenzonitrile, b.p. 80—85°/11 mm., but in presence of (II)-dioxan at 20—25° give hexa- $\beta$ -cyanoethylcyclopentadiene, m.p. 203°, and liquids, b.p. 100—280°/1 mm. Similarly, dimethylfulvene and (I) alone give 2: 5-endo- $\Delta^1$ -isobutenylidene- $\Delta^3$ -tetrahydrobenzonitrile, m.p. 87°, b.p. 95—100°/1 mm., but in presence of (II) give impure  $\beta$ -cyanoethyl derivatives.  $\omega\omega$ -Dimethylbenzofulvene with (I) and (II) in dioxan at 25—35° gives a  $\beta$ -cyanoethyl derivative, m.p. 121°, but Diels-Adler products are resinous. Alkaline hydrolysis converts the products into 9: 9-di- $\beta$ -carboxyethylfluorene, m.p. 273—274°, 1: 1: 3-tri- $\beta$ -carboxyethylindene, m.p. 161—162°, 9: 9-di- $\beta$ -carboxyethylanthr-10-one, sinters 220°, decomp. 230°, and hexa- $\beta$ -carboxyethylcyclopentadiene, m.p. 180—181°. CH<sub>2</sub>:CH·CO<sub>2</sub>R (R = Me or Et) does not replace (I), but with (III) undergoes Diels-Alder reaction giving Me, b.p. 71—73°/8 mm., or Et 2: 5-endomethylene- $\Delta^3$ -tetrahydrobenzoate, b.p. 84—85°/10 mm. CHMe:CH·CN with (II) and indene or (III) gives resinous products, but with fluorene gives 9- $\beta$ -cyanoisopropylfluorene, m.p. 92—93°. R. S. C.

**Preparation of aromatic dinitriles.**—See B., 1943, II, 45.

**Esters of  $\Delta^1$ -tetrahydrophthalic acid.**—See B., 1943, II, 44.

**Stereochemistry of catalytic hydrogenation. I. Stereochemistry of the hydrogenation of aromatic rings.** R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone. **II. Preparation of the six inactive perhydrodiphenic acids.** **III. Optically active perhydrodiphenic acids. Proof of the configuration of the backbone.** R. P. Linstead, W. E. Doering, and (in part) F. H. Slinger. **IV. Hexahydrodiphenic acids.** R. P. Linstead and S. B. Davis. **V. Assignment of *cis* and *trans* configurations.** R. P. Linstead, S. B. Davis, and R. R. Whetstone. **VI. Hydrogenation of 9-phenanthrol and related substances. Identification of three of the possible stereoisomeric forms of the perhydrophenanthrene ring.** R. P. Linstead, R. R. Whetstone, and P. Levine. **VII. Complete hydrogenation of phenanthraquinone.** R. P. Linstead and P. Levine (*J. Amer. Chem. Soc.*, 1942, **64**, 1985—1991, 1991—2003, 2003—2006, 2006—2009, 2009—2014, 2014—2022, 2022—2026).—I. Theoretical. Nomenclature and structural representation are those previously proposed [A., 1939, II, 307; cf. (I) and (V) below]. For, e.g., hydrogenated 9-phenanthrones and Me H diphenates etc. the configuration of the C<sub>6</sub>-ring adjacent to the CO, CO<sub>2</sub>Me, etc. is named first. In work described below (9 cases) and in the literature (reviewed), complete hydrogenation of mono-, di-, and tri-cyclic aromatic hydrocarbons, OH-compounds, acids, and derivatives of acids in presence of PtO<sub>2</sub> at room temp. gives mainly *cis*- and *syn*-derivatives, e.g., (I). This unilateral addition of H<sub>2</sub> is due to (a) complete hydrogenation occurring during a single period of adsorption on the catalyst, (b) "catalyst hindrance" (see below), and (c) diphenic acid etc. being hydrogenated in the coiled phase, i.e., with the CO<sub>2</sub>R contiguous. Catalyst hindrance occurs when the configuration of the reactant-catalyst adsorption complex is such that the surface of the catalyst prevents access of the reagent to some portion of the reactant; it is shown diagrammatically to reduce *trans* and *anti* addition of H in the phenanthrene and diphenic acid series.

II. Configurations assigned below are proved in later work. The six possible dodecahydrodiphenic acids are prepared; three other acids so described previously are accounted for. *cis-syn-cis*-Dodecahydrodiphenic acid (I), m.p. 287—289° (varies with the rate of heating) (Linstead *et al.*, A., 1939, II, 322; Vocke, A., 1934, 189; m.p. 273°), is half-inverted by way of the Me H ester to the *cis-syn-trans-acid* (II), dimorphic, m.p. 199—200° and 173—175°, and completely inverted by acid at high temp. to the *trans-syn-trans-*



acid (III), m.p. 221—223° (*loc. cit.*, 200°). Similarly, the *cis-anti-cis-acid* (IV), m.p. 197—198.5°, gives the *cis-anti-trans-* (V), m.p.

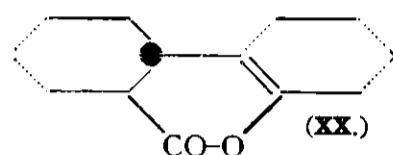
205.5–206.5°, and *trans-anti-trans*-acid (VI), sinters at 237°, m.p. 246–248° (*loc. cit.*, 244°). When *cis*-Me H (or Me<sub>2</sub>) esters are hydrolysed by KOH–MeOH, inversion to the more stable *trans*-form occurs only at the C adjacent to CO<sub>2</sub>Me. Diphenic acid (VII) (modified prep.; Me H ester, m.p. 110–111°) with H<sub>2</sub>–PtO<sub>2</sub> in AcOH at 60 lb. gives (I) (53%), (IV) (10%), (II) (7%), *cis*-1:2:3:4:5:6-hexahydrodiphenic acid (VIII) (10%), m.p. 241–242° (bath initially at 235°) (*cf. loc. cit.*), and unchanged (VII) (20%); the by-products are separated by fractional acidification of the Na salts in H<sub>2</sub>O at the b.p., followed by orthodox methods. Hydrogenation in EtOH is slower but also gives mainly (I). The anhydride, new m.p. 146–147°, of (I) with NaOMe–MeOH at room temp. gives the *cis-syn-cis*-Me H ester (IX) (76.5%), m.p. 128.5–129.5°, and with boiling MeOH + a drop of 15% oleum gives (IX) (30%) and the *cis-syn-cis*-Me<sub>2</sub> ester (X), m.p. 73–74°. In boiling MeOH + 2% of 15% oleum, (I) gives 95% of (X) and 2.5% of (IX), with CH<sub>2</sub>N<sub>2</sub> (excess) in dioxan gives (X) (89%), or with CH<sub>2</sub>N<sub>2</sub>–EtOH (1 equiv.) gives also some (IX). CH<sub>2</sub>N<sub>2</sub>–Et<sub>2</sub>O converts (IX) into (X). Boiling conc. HCl–AcOH hydrolyses (IX) or (X), without inversion, to (I); aq. 20% NaOH also hydrolyses (IX) to (I). Boiling NaOMe–MeOH followed by a little H<sub>2</sub>O partly inverts and then hydrolyses (IX), yielding (II). KOH in boiling commercial MeOH causes complete inversion of (X), yielding (III). NaOMe in boiling, freshly dried MeOH converts (IX) by half-inversion without hydrolysis into the *trans-syn-cis*-Me H ester (XI), m.p. 97–99°; this change is very facile, for MeOH distilled from BaO may contain enough alkali to convert the anhydride of (I) into (XI). CH<sub>2</sub>N<sub>2</sub> (excess) converts (II) or (XI) into the *trans-syn-cis*-Me<sub>2</sub> ester (XII), m.p. 12.5–14.5°, hydrolysed by boiling conc. HCl–AcOH to (II) and the *cis-syn-trans*-Me H ester, m.p. 101.5–102.5°. Boiling Ac<sub>2</sub>O converts (II) into the *cis-syn-trans*-anhydride, m.p. 104–104.5° (*cf. Marvel et al.*, A., 1941, II, 15), and some oily polymeride, both reconverted into (II) by boiling aq. alkali. CH<sub>2</sub>N<sub>2</sub> converts (III) into the *trans-syn-trans*-Me<sub>2</sub> ester (XIII), m.p. 56–57.5°, reconverted into (III) by boiling HCl–AcOH. The *trans-syn-trans*-anhydride [prep. from (III) by Ac<sub>2</sub>O], m.p. 105–106.5°, in boiling dry MeOH gives the *trans-syn-trans*-Me H ester, m.p. 115.5–117.5°, converted by acid or (poor yield) alkali into (III), and by CH<sub>2</sub>N<sub>2</sub> into (XIII). Boiling NaOMe–MeOH completely inverts (X), without hydrolysis, yielding (XIII), which is also obtained by partial inversion and hydrolysis of the *cis-syn-trans*-Me H ester by KOH–MeOH. With boiling Ac<sub>2</sub>O, (IV) gives the *cis-anti-cis*-anhydride, forms, m.p. 95–96° and 99–100°, and thence (MeOH) the *cis-anti-cis*-Me H ester (XIV), m.p. 97.5–99°, converted by CH<sub>2</sub>N<sub>2</sub> [as is (IV)] into the *cis-anti-cis*-Me<sub>2</sub> ester (XV), m.p. 43–44.5°; both esters are hydrolysed by HCl–AcOH to (IV). KOH–MeOH converts (XIV) (inversion) into (V) (*anhydride*, m.p. 91.5–93°) and (XV) into (VI) (Me<sub>2</sub> ester, m.p. 84.5–86°). The acid, m.p. 213°, of Vocke (*loc. cit.*) is probably impure (III). The acid, m.p. 174°, of Marvel *et al.* (*loc. cit.*) is a dimorph of (II). The acid, m.p. 203°, of Linstead *et al.* (*loc. cit.*) is *dodecahydrodiphenyl-1:2'-dicarboxylic acid*; its predecessors, the unsaturated ketones, m.p. 94° and 39°, have the spiran structures proposed by Woodward (A., 1942, II, 164), and the saturated ketones are the *cis*- and *trans*-forms of the *perhydrospirans*.

III. In the *syn*-series of dodecahydrodiphenic acids only the intermediate *cis-trans*-form is resolvable; in the *anti*-series all three forms are resolvable. Prep. of active forms of (II), (IV), and (VI), and resistance of (I) and (III) to resolution prove the configurations assigned above to (I)–(VI). Five alkaloidal salts of (I) were cryst. but regenerated inactive acids. Its Me H ester (IX) is, however, resolved by cinchonidine into the *l*- and *d*-Me H esters, m.p. 133.5–134.5°,  $[\alpha]_D^{27} -10.7 \pm 0.3^\circ$ ,  $+10.3 \pm 0.3^\circ$  in 95% EtOH. The *l*-ester is hydrolysed by conc. HCl–AcOH to (I),  $\alpha$  0, and with CH<sub>2</sub>N<sub>2</sub> gives (X),  $\alpha$  0, thus conclusively proving the *meso*-nature of (I). With NaOMe–MeOH at room temp. (later a little H<sub>2</sub>O is added), the *l*- and *d*-esters give, by partial inversion and hydrolysis, the *d*-, m.p. 170–174°,  $[\alpha]_D^{29} +75^\circ$ , and *l*-, m.p. 171–174°,  $[\alpha]_D^{28} -75^\circ$  in EtOH, *cis-syn-trans*-acids, respectively. (III) (brucine salt, cryst.) resists resolution. Cinchonidine yields the *l*-, m.p. 239–241°,  $[\alpha]_D^{26} -45 \pm 1^\circ$  (cinchonidine salt, m.p. 204.5–205.5°), and *d-cis-anti-cis*-acid (XVI), m.p. 238.5–240.5°,  $[\alpha]_D^{27} +43 \pm 1^\circ$  in 95% EtOH. The Me<sub>2</sub> ester (CH<sub>2</sub>N<sub>2</sub>), m.p. 26–28°,  $[\alpha]_D^{26} +69 \pm 1^\circ$  in 95% EtOH, of (XVI) is inverted by boiling KOH–MeOH, yielding the *l*-form, m.p. 257–258.5°,  $[\alpha]_D^{26} -79.5 \pm 5^\circ$  in 95% EtOH, of the *trans-anti-trans*-acid; the *d*-form, m.p. 257.5–259°,  $[\alpha]_D^{20} +77.5^\circ$  in EtOH, is prepared by way of the ephedrine salt of the acid and with the *l*-form regenerates (VI).

IV. Absorption of 3 H<sub>2</sub> by (VII) in presence of PtO<sub>2</sub> in AcOH yields (I) (25%), (VIII) (25%), and unchanged (VII) (40%). H<sub>2</sub>–PtO<sub>2</sub> in AcOH converts (VIII) into (I) (77%), reaction being again homogeneously *cis-syn* in contrast to the results of Vocke (*loc. cit.*) using Ni. The presence of an aromatic ring in (VIII) is proved by prep. of a NO<sub>2</sub>-derivative, dimorphic, m.p. 201–202° and 218–219° (yields an amine which diazotises and couples with  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH). In boiling Ac<sub>2</sub>O, (VIII) yields an oily anhydride, regenerating (VIII) by hydrolysis (boiling dil. HCl). At the m.p., (VIII) is isomerised to the *trans*-hexahydrodiphenic acid (XVII), m.p. 220–221.5° (NO<sub>2</sub>-derivative, forms, m.p. 218–219° and 224–

225°) (*cf. Vocke, loc. cit.*), best purified by way of the *anhydride* (XVIII), m.p. 115–116°. At 243±3° (XVIII) is equilibrated with the *cis*-form, but 70% of (XVIII) is recovered; some CO<sub>2</sub> is evolved. Hydrogenation of (XVII) yields homogeneously (<84%) (II).

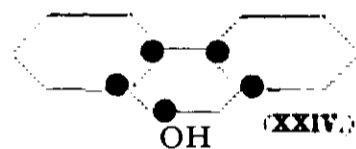
V. The following and known reactions prove the *cis*-configuration of (VIII), (I), and (IV), and the *trans*-configuration of (XVII), (III), and (VI), and correlate the 9-keto-*as*-octahydrophenanthrenes with the hexahydrodiphenic acids. Oxidation of (VIII) by HNO<sub>3</sub> or KMnO<sub>4</sub> was unsuccessful, but by O<sub>3</sub> in AcOH (later H<sub>2</sub>O<sub>2</sub>) gives *cis*-hexahydrophthalic [*cyclohexane-1:2*-dicarboxylic] acid, separated from unchanged (VIII) by partial acidification of the salt and identified by conversion into the dianilide, m.p. 237.5–238° (lit. 234°), and phenylimide, m.p. 132°; the dianilide, m.p. 317–318°, of *trans*-hexahydrophthalic acid (XIX), new m.p. 227–229° (preheated to 200°), yields no phenylimide. The structure of 9-keto- $\Delta^{10}$ -dodecahydrophenanthrene and its precursors (Rapson *et al.*, A., 1935, 1498) is proved by ozonisation in



AcOH to give *trans*-2-ketodicyclohexyl-2'-carboxylic acid, an oil (*oxime*, m.p. 162–163°), converted by Ac<sub>2</sub>O into the oily lactone (XX), which with KMnO<sub>4</sub>–NaHCO<sub>3</sub>–COMe<sub>2</sub>–H<sub>2</sub>O gives (XIX), m.p. 227–229° (bath initially at 200°) (*cf. lit.*).

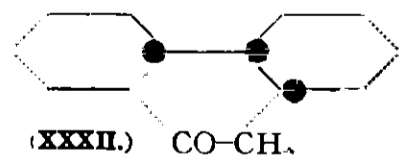
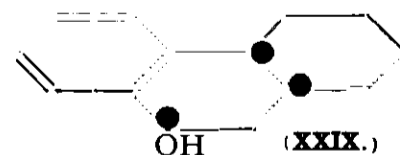
The liquid *cis*-9-keto-1:2:3:4:9:10:11:12-octahydrophenanthrene (XXI) (Cook *et al.*, A., 1936, 334; 1939, II, 103) gives, according to the conditions, a (NO<sub>2</sub>)<sub>2</sub>-, m.p. 95–96.5°, or (NO<sub>2</sub>)<sub>3</sub>-derivative, m.p. 151.5–152°, the latter product being accompanied by the NO<sub>2</sub>-derivative (above) of (VIII) (proof of structure). *trans*-9-Keto-1:2:3:4:9:10:11:12-octahydrophenanthrene (XXII) gives a (NO<sub>2</sub>)<sub>3</sub>-derivative, m.p. 182.5–183.5°, and the NO<sub>2</sub>-derivative of (XVII).

VI. Pt-hydrogenation of phenanthrene hydrocarbons, alcohols, and ketones is substantially *cis-syn*. 9-Phenanthrol (XXIII) (modified prep.) with H<sub>2</sub>–PtO<sub>2</sub> in AcOH gives a hydrocarbon, b.p. 121°/3 mm., *cis-syn-cis-tetradecahydro-9-phenanthrol* (XXIV), m.p. 110.5–111°, and a small amount of 1:2:3:4:5:6:7:8-octahydro-9-phenanthrol (XXV), m.p. 134.5–135°; H<sub>2</sub>–Raney Ni in EtOH at 120°/123 atm. gives mainly (XXV) (best method of prep.) (*cf. von Braun et al.*, A., 1926, 172; m.p. 133°), which is obtained



also with difficulty from Na *s*-octahydrophenanthrene-9-sulphonate and KOH at 290–300°. (XXIV) is converted into (I) by HNO<sub>3</sub> at 100° and thus has the configuration stated; configuration at C<sub>9</sub> is uncertain, but on the hypothesis of

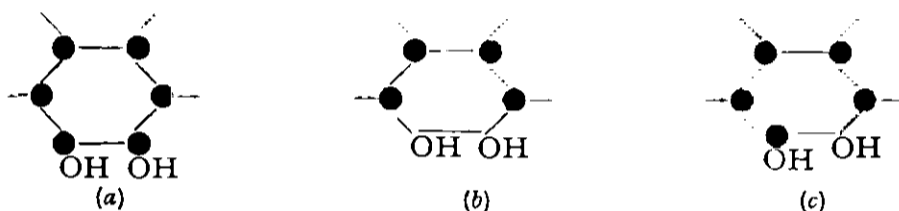
catalyst hindrance is as shown. 2-Phenylcyclohexanone (XXVI) and CH<sub>2</sub>Br·CO<sub>2</sub>Et give the OH-ester (80%), and thence (PCl<sub>5</sub>–C<sub>6</sub>H<sub>6</sub>) an unsaturated ester (77%), b.p. 146–153°/3 mm., and 2-phenyl- $\Delta^1$ -cyclohexenylacetic acid (93%), m.p. 92–93°, hydrogenated (Pd–AcOH) to *cis*-2-phenylcyclohexylacetic acid (XXVII), m.p. 168–170°, and some of the *trans*-isomeride, m.p. 113.5–114.5° (XXVIII) (not isolated); in H<sub>2</sub>SO<sub>4</sub>, pure (XXVII) gives (XXI); the mother-liquors from (XXVII) give (XXII) (*cf. Cook et al., loc. cit.*). 1-Hydroxy-2-phenylcyclohexylacetic acid (prep. by hydrolysis of the ester; 75%), m.p. 128–129°, with Ac<sub>2</sub>O (*cf. loc. cit.*) gives 17% but with boiling (Pr<sup>o</sup>CO)<sub>2</sub>O gives 35% of 2-phenylcyclohexylideneacetic acid, m.p. 168–170° [with KMnO<sub>4</sub> gives (XXVI); equilibration by alkali gives mainly the  $\Delta^{\beta\gamma}$ -acid]; hydrogenation thereof is usually *cis*, giving (XXVII), but in presence of Pd in C<sub>6</sub>H<sub>6</sub> gives 33% of (XXVIII) (best method of prep.) with 57% of (XXVII). With 1 H<sub>2</sub> in presence of EtOH, (XXI) gives 93% of *cis*-1:2:3:4:9:10:11:12-octahydro-9-phenanthrol (XXIX), m.p. 115–116° (*loc. cit.*, m.p. 114–115°), which probably (catalyst hindrance) has the structure shown;



however, (XXII) gives varying amounts of C<sub>9</sub>-epimeric *trans*-1:2:3:4:9:10:11:12-octahydro-9-phenanthrols, m.p. 90–91° and 100–101°. Na–EtOH reduces (XXI) to a mixture, including (XXIX); Al(OPr<sup>o</sup>)<sub>3</sub>–Pr<sup>o</sup>OH gives an inseparable mixture; H<sub>2</sub> (1.95 mols.)–Pd in EtOH gives mainly (?) *cis*-1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p. 121–122°/4–5 mm. (lit. 129°/6 mm.), and a little (XXIX). Perhydrogenation of (XXI) or (XXIX) often leads to elimination of O; e.g., with H<sub>2</sub>–PtO<sub>2</sub> in EtOH + (little) AcOH it gives a hydrocarbon, b.p. 109–111°/4 mm., with a little (XXIV). With H<sub>2</sub> (3.4 mols.) and PtO<sub>2</sub> in EtOH, (XXI) gives (XXIV), (XXIX), an *epimeride* (XXX), m.p. 132.5–133.5°, of (XXIX), and a mixture (A), m.p. 85–87°, which yields (XXIV) (10%), (XXIX) (10%), and (XXX) (30%); similar perhydrogenation of (XXIX) gives (XXIV) (47%) and (A) (10%). CrO<sub>3</sub>–AcOH at 0° (later room temp.) oxidises (XXIV) to *cis-syn-cis*-9-ketotetradecahydrophenanthrene (XXXI), m.p. 43–44°, but at 100° gives the *trans-syn-cis*-isomeride (XXXII), m.p. 56.5–57.5° [*oxime*, m.p. 224–225°, regenerates (XXXII)]; Al(OBu<sup>o</sup>)<sub>3</sub>–COMe<sub>2</sub>–C<sub>6</sub>H<sub>6</sub> gives a mixture. Structures are proved by oxidation (HNO<sub>3</sub>) of (XXXI)

to (I) and of (XXXII) to (II). Relations of (XXXI) and (XXXII) parallel those of the 1-ketodecahydronaphthalenes: boiling NaOEt-EtOH effects the change, (XXXI)  $\rightarrow$  (XXXII); (XXXI) gives an oxime, m.p. 150—151°, unstable in hot EtOH, but gives directly the 2:1-dinitrophenylhydrazone, m.p. 236—238° (decomp.), of (XXXII).  $H_2$ -PtO<sub>2</sub> in EtOH reduces (XXXII) to trans-syn-cis-tetradecahydro-9-phenanthrol, m.p. 88—89°. The ketone, m.p. 57°, of Marvel *et al.* (A., 1941, II, 15, 357) was (XXXII), but its precursor, the alcohol, m.p. 67°, is of uncertain structure. CN·CH<sub>2</sub>·CO<sub>2</sub>Et, (XXVI), and NH<sub>4</sub>OAc in C<sub>6</sub>H<sub>6</sub>-AcOH at 140—160° give crude Et 2-phenylcyclohexylidenecyanoacetate (54%), b.p. 174°/4 mm. [by reduction ( $H_2$ -PtO<sub>2</sub>-EtOH or Al-Hg-Et<sub>2</sub>O) and then hydrolysis gives (XXVII)], containing some 10-cyano-1:2:3:4-tetrahydro-9-phenanthrol (8%), m.p. 230—231° [benzoate, m.p. 183—184°; picrate, m.p. 185—190° (decomp.)]; Na salt, formed by aq. Na<sub>2</sub>CO<sub>3</sub>; resists hydrolysis; the latter product is obtained from the former by heating at 200—220°.

VII. Hydrogenation (Pt; Ni) of phenanthraquinone (modified prep. and purification) gives mainly *cis-syn* compounds.  $H_2$ -PtO<sub>2</sub> in AcOH at 4 atm. gives slowly  $\alpha$ -*cis-syn-cis*-tetradecahydrophenanthrene-9:10-diol (XXXIII), m.p. 173.9—174.4° (dibenzoate, m.p. 153.5—154°, prep. in C<sub>5</sub>H<sub>5</sub>N). In presence of Raney Ni in EtOH at 110°/80 atm., 6 mols. of H<sub>2</sub> are absorbed (cf. von Braun *et al.*, *loc. cit.*), but at 160°/170 atm. 8 mols. are absorbed, yielding, from 26 g.,  $\beta$  (7.54 g.), m.p. 173.9—174.4° [depresses the m.p. of (XXXIII)] (dibenzoate, m.p. 115.5—116°), and  $\gamma$ -*cis-syn-cis*- (XXXIV) (3.96 g.), m.p. 154.5—155.5° (dibenzoate, m.p. 114.2—115°), and  $\alpha$ -*cis-syn-trans*-tetradecahydrophenanthrene-9:10-diol (XXXV) (0.138 g.), m.p. 184—184.5°. By  $H_2$ -Raney Ni in EtOH at 120°, 9:10-dihydroxy-decahydrophenanthrene, m.p. 135—136° (diacetate, m.p. 160—161°) (cf. Skita, A., 1926, 173), is obtained. All the diols give Criegee's test for 1:2-diols. The structures of the *cis-syn-cis*-diols are proved by oxidation [Pb(OAc)<sub>4</sub>-C<sub>6</sub>H<sub>6</sub>, KIO<sub>4</sub>, CrO<sub>3</sub>-AcOH, or AcO<sub>2</sub>H; less well, Beckmann's mixture; not KMnO<sub>4</sub>, HNO<sub>3</sub>, or KBr] to (I); the formulæ (a) (*meso*), (b) (*meso*), and (c) (*dl*) are



available for the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -diols, but the precise allocation thereof is unknown. Similar oxidation to (II) proves the *cis-syn-trans* structure of (XXXV), for which four formulæ (all *dl*), differing at C<sub>(9)</sub>-C<sub>(10)</sub>, are available. Dehydration of the diols by activated or pptd. Al<sub>2</sub>O<sub>3</sub> gives only a trace of ketone; (XXXIV) with KHSO<sub>4</sub> at 150—160° gives a compound, (C<sub>14</sub>H<sub>22</sub>O)<sub>x</sub> ( $x$  may be 1), m.p. 202—203°, and a substance giving a crude oxime, m.p. 190—200°. M.p. (all parts) are corr. R. S. C.

**Dehydration of  $\alpha\beta$ -distyryl[ethylene] glycol by sulphuric acid. Formation of  $\gamma$ -phenyl- $\alpha$ -styryl- $\Delta^2$ -butenaldehyde by a hydrobenzoin change followed by displacement of a double linking.** Y. Deux (*Compt. rend.*, 1942, 214, 269—271).—[CHPh·CH·CH(OH)]<sub>2</sub>, m.p. 158° (? di-*p*-nitrobenzoate, m.p. 186°), obtained by reduction of CHPh·CH·CHO with Zn-Cu in aq. EtOH, is converted by boiling 20% H<sub>2</sub>SO<sub>4</sub> into  $\gamma$ -phenyl- $\alpha$ -styryl- $\Delta^2$ -butenaldehyde (I), b.p. 158—160°/5 mm. (semicarbazone, m.p. 210—211°; oxime, m.p. 135—136°). (I) is oxidised (KMnO<sub>4</sub>) to BzOH and CH<sub>2</sub>Ph·CO<sub>2</sub>H, and hydrogenated (Raney Ni) to (Ph·[CH<sub>2</sub>]<sub>2</sub>)<sub>2</sub>CH·CHO (semicarbazone, m.p. 155—156°; oxime, m.p. 98—99°), which is oxidised (Ag<sub>2</sub>O) to the corresponding acid, b.p. 210—212°/4 mm. (amide, m.p. 165°; anilide, m.p. 150°), also obtained by decarboxylation of (Ph·[CH<sub>2</sub>]<sub>2</sub>)<sub>2</sub>C(CO<sub>2</sub>H)<sub>2</sub>. J. E. P.

**ortho-Alkylation and -arylation of mesityl aryl ketones.** R. C. Fuson and S. B. Speck (*J. Amer. Chem. Soc.*, 1942, 64, 2446—2448).—The OMe of *o*-methoxyaryl mesityl ketones is replaced by R by treatment with MgRHal. 2:4:6:1-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>·COCl (I), the appropriate aryl compound, and AlCl<sub>3</sub> in CS<sub>2</sub> at room temp. give 4-methoxy-*m*-tolyl (II), m.p. 103°, 2-methoxy-1-naphthyl (III), m.p. 109—110°, and *m*-anisyl mesityl ketone (IV), m.p. 76°. *o*-Anisyl mesityl ketone (V), m.p. 112—113°, is obtained from *o*-OMe·C<sub>6</sub>H<sub>4</sub>·MgBr and (I) in Et<sub>2</sub>O. With Et<sub>2</sub>O·C<sub>6</sub>H<sub>5</sub>·MgPhBr at 30° or 60°, (V) gives *o*-diphenyl (VI) (35%), m.p. 89° (cf. A., 1942, II, 315), or 2:6-diphenylphenyl mesityl ketone (VII) (20%), m.p. 162°, respectively; 2.5% and traces of (VII) are obtained from MgPhBr with 2:4:6:1-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>·CO·C<sub>6</sub>H<sub>4</sub>Br-*o* and (VI), respectively. The product (A., 1942, II, 311) from (V) and *o*-OMe·C<sub>6</sub>H<sub>4</sub>·MgBr is 2-methoxy-2'-mesityldiphenyl. With MgPhBr, (II) affords 4-phenyl- (18%), m.p. 73°, and 2:4-diphenyl- (20%), m.p. 131°, and with MgEtBr gives 4-ethyl- (28%), m.p. 58°, -*m*-tolyl mesityl ketone. MgRHal and (III) give 2-phenyl- (59%), m.p. 136°, 2-*a*-naphthyl- (76%), m.p. 181°, 2-methyl- (56%), m.p. 67° (also obtained from 2:1-C<sub>10</sub>H<sub>6</sub>Me·COCl by C<sub>6</sub>H<sub>5</sub>Me<sub>3</sub>-AlCl<sub>3</sub> or C<sub>6</sub>H<sub>5</sub>Me<sub>3</sub>·MgBr), 2-ethyl- (80%), m.p. 90°, and 2-*n*-butyl-1-naphthyl mesityl ketone (55%), m.p. 73°. MgPhBr and (IV) give a little (?) mesityl 4-methoxy-2-diphenyl ketone, m.p. 194—195° (corr.). R. S. C.

**Effect of methoxyl toward stabilising ene-diols.** R. P. Barnes and W. M. Lucas (*J. Amer. Chem. Soc.*, 1942, 64, 2258—2259).—*p*-OMe has a greater stabilising effect on benzoin and the enediol than has *o*-OMe. 2:2'-Dimethoxybenzoin (I) with Ac<sub>2</sub>O-KOAc at 100° gives the acetate, m.p. 102°, converted by further boiling into a little  $\alpha\beta$ -diacetoxy- $\alpha\beta$ -di-*o*-anisylethylene (II), m.p. 149°, stable to boiling KOAc-AcOH, but hydrolysed by boiling H<sub>2</sub>SO<sub>4</sub>-aq. EtOH (not conc. H<sub>2</sub>SO<sub>4</sub>-N<sub>2</sub> at 0°) to (I). However, 4:4'-dimethoxybenzoin gives an acetate, m.p. 93.5°, not convertible into the Ac<sub>2</sub> compound.  $\alpha\beta$ -Diacetoxy- $\alpha\beta$ -di-*p*-anisylethylene [prep. from (*p*-OMe·C<sub>6</sub>H<sub>4</sub>·CO)<sub>2</sub> (III) by  $H_2$ -PtO<sub>2</sub>-ZnCl<sub>2</sub>-Ac<sub>2</sub>O; (II) is similarly obtained], m.p. 121—124°, is converted by conc. H<sub>2</sub>SO<sub>4</sub> at room temp., by hydrolysis and oxidation, into (III). R. S. C.

**Preparation and properties of an ene-diol.  $\beta$ -Mesityl- $\alpha$ -*o*-anisyl-acetylene glycol.** R. P. Barnes and W. M. Lucas (*J. Amer. Chem. Soc.*, 1942, 64, 2260—2261).—*o*-OMe stabilises an ene-diol. Mesityl *o*-methoxystyryl ketone (prep. from *o*-OMe·C<sub>6</sub>H<sub>4</sub>·CHO and 2:4:6:1-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>·COMe in NaOH-H<sub>2</sub>O-EtOH), m.p. 95°, with warm H<sub>2</sub>O<sub>2</sub>-NaOH-H<sub>2</sub>O-EtOH gives the oxide, m.p. 73—74°, converted by NaOH in boiling aq. EtOH into mesityl  $\alpha$ -hydroxy-*o*-methoxystyryl ketone, m.p. 137° [red FeCl<sub>3</sub> colour; 98% enolic (Kurt Meyer)]. With Br-CaCO<sub>3</sub> in CCl<sub>4</sub> this gives HBr and  $\alpha$ -bromo- $\beta\gamma$ -diketo- $\alpha$ -*o*-anisyl- $\gamma$ -mesitylpropane (I), m.p. 84° (non-enolic), converted by boiling KOAc-AcOH into mesityl  $\alpha$ -hydroxy- $\beta$ -acetoxy-*o*-methoxystyryl ketone (II), m.p. 94° (red FeCl<sub>3</sub> colour; 84% enolic). The  $\alpha\beta$ -diacetate (III), m.p. 103—104°, is obtained from (II) by AcCl or from (I) and Ac<sub>2</sub>O-KOAc. Conc. H<sub>2</sub>SO<sub>4</sub> at 0° hydrolyses (II) or (III) to mesityl  $\alpha\beta$ -dihydroxy-*o*-methoxystyryl ketone, m.p. 105°, which gives a bluish-green FeCl<sub>3</sub> colour, decolorises I and 2:6-dichlorobenzene-indophenol, giving in all cases (slowly in air) *o*-anisyl mesityl diketone, m.p. 132°, which with H<sub>2</sub>O<sub>2</sub>-alkali yields *o*-anisic and mesitoic acids (proof of structure). R. S. C.

**Properties of *o*-anisylmesitylmethane.** R. P. Barnes and C. C. Cochrane (*J. Amer. Chem. Soc.*, 1942, 64, 2262).—*o*-Anisyl 2:4:6-trimethylstyryl ketone, m.p. 118°, gives a dibromide, m.p. 135°, converted by boiling NaOMe-MeOH into *o*-anisyl  $\beta$ -methoxy-2:4:6-trimethylstyryl ketone, m.p. 87°, which with boiling conc. HCl-MeOH gives the  $\beta$ -OH-derivative [=mesityl  $\beta$ -hydroxy-*o*-methoxystyryl ketone] (I), m.p. 105°. 2:4:6:1-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>·CO·CH:CH·C<sub>6</sub>H<sub>4</sub>·OMe-*o* gives similarly its dibromide, m.p. 86°, mesityl  $\beta$ :*o*-dimethoxystyryl ketone, m.p. 85°, and (I). (I) gives a red FeCl<sub>3</sub> colour, is 100% enolic, but is unaffected by CH<sub>2</sub>N<sub>2</sub>, Ac<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub>, or AcOH. This and its dual mode of formation indicate its existence as a chelate compound. R. S. C.

**Stereoisomeric unsaturated bromo- $\alpha\delta$ -dimesityl  $\alpha\delta$ -diketones.** R. E. Lutz and D. H. Terry (*J. Amer. Chem. Soc.*, 1942, 64, 2426—2430).—Yellow trans-COR·CBr:CH·COR (I) (R = mesityl here and below) (best prep.: A., 1925, i, 681) is obtained from (COR·CHBr)<sub>2</sub> by boiling NaOBz-EtOH or AgOBz-Pr<sub>2</sub>O and is converted by illumination in EtOH into a colourless *cis*-form, m.p. 88—89°, whence it is regenerated by illumination in CHCl<sub>3</sub>-I. Both forms are converted by KI-AcOH into trans-(COR·CH)<sub>2</sub> (II), by boiling KOH-70% EtOH into COR·C(OH):CH·COR, and by NaOMe-MeOH at room temp. into *cis*-COR·C(OMe):CH·COR, and are unchanged by Ac<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> at 100°. Boiling HCl-AcOH-H<sub>2</sub>O does not affect (I). PhICl<sub>2</sub> and (II) in CHCl<sub>3</sub> at room temp. give (COR·CHCl)<sub>2</sub> (39%), m.p. 209° (decomp.) (cf. A., 1927, 58), which in boiling EtOH gives COR·CCl:CH·COR, also obtained from [COR·CH(OH)]<sub>2</sub> by PCl<sub>5</sub>-CHCl<sub>3</sub>. PhICl<sub>2</sub> and (II) in boiling CHCl<sub>3</sub> give a nuclear-chlorinated, unsaturated diketone, C<sub>22</sub>H<sub>22</sub>O<sub>2</sub>Cl<sub>2</sub>, m.p. 209.5—210°, converted by Zn dust-AcOH into a Cl-containing compound, m.p. 166—167°. trans-COR·CMe:CH·COR (III) (improved prep.; stable to light in MeOH) with Br-CHCl<sub>3</sub> at -10° gives slowly HBr and small amounts of *cis*- $\beta$ -bromo- $\alpha\delta$ -dimesityl- $\gamma$ -methyl- $\Delta^2$ -butene- $\alpha\delta$ -dione (IV), m.p. 143.5—144°,  $\beta\gamma$ -tribromo- $\alpha\delta$ -dimesityl- $\gamma$ -methylbutane- $\alpha\delta$ -dione (V), m.p. 188°, and  $\alpha\delta$ -dimesityl- $\beta$ -methylbutane- $\alpha\delta$ -dione (VI), m.p. 60.5°. Removal of HBr by NaHCO<sub>3</sub> during bromination at 0° leads to 77.7% of (IV). With boiling NaOBz- or NaOAc-EtOH, AgOBz-Pr<sub>2</sub>O, or 1:1 C<sub>5</sub>H<sub>5</sub>N-H<sub>2</sub>O, (IV) gives the trans-isomeride (VII), m.p. 171—171.5°. (VI) is obtained from (III) by SnCl<sub>2</sub>-HCl-AcOH or H<sub>2</sub>-Pt or from (VII) by Zn dust-AcOH at room temp.; it could not be cyclised. In AcCl + a trace of H<sub>2</sub>SO<sub>4</sub>, (III) gives 4-acetoxy-2:5-dimesityl-3-methylfuran, m.p. 88°. R. S. C.

**Preparation and alkylation of  $\alpha\delta$ -dimesityl- $\gamma$ -methylbutane- $\alpha\beta\delta$ -trione enol.** R. E. Lutz and D. H. Terry (*J. Amer. Chem. Soc.*, 1942, 64, 2423—2426).—*cis*-COR·CBr:CH·COR (I) (R = mesityl here and below) with NaOH in boiling 90% MeOH gives  $\beta$ -hydroxy- $\alpha\delta$ -dimesityl- $\gamma$ -methyl- $\Delta^2$ -butene- $\alpha\delta$ -dione (II) (64%), m.p. 124.5—125° (sol. Na and insol. unstable Ag salt; no CO derivative; maroon colour with FeCl<sub>3</sub>-EtOH; sol. in aq. Na<sub>2</sub>CO<sub>3</sub>) (cf. A., 1942, II, 408), but in 80% MeOH gives largely non-cryst. material with 30% of a Br-free compound, m.p. 234°. With CH<sub>2</sub>N<sub>2</sub>-Et<sub>2</sub>O, (II) gives the *cis*- $\beta$ - (III) (44%), m.p. 134.5—135°, and trans- $\beta$ -Me ether (IV) (9%), m.p. 156.5—157°, trans- $\delta$ - (V) (30%), m.p. 119.5—120°, and *cis*- $\delta$ -Me ether (VI) (15%), m.p. 142°. (II) is also obtained from COR·C(OAg):CH·COR by MeI in boiling Pr<sub>2</sub>O (7% yield),

from (III) or (IV) by HCl-AcOH-H<sub>2</sub>O at room temp., or from (V) or (VI) at the b.p. The Ag salt of (II) with MeI-MeOH-H<sub>2</sub>O at

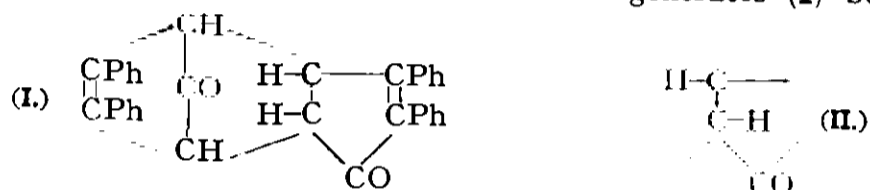


0–60° gives 65% of (V) and 37% of *α*-dimethyl-ββ-dimethylbutane-*α*-trione, m.p. 132.5–133° unaffected by boiling HCl-AcOH-H<sub>2</sub>O or NH<sub>2</sub>OH-MeOH. With NaOMe-MeOH at room temp., (I) gives 58% of (III) and 12% of (IV). Boiling HCl-MeOH converts (III) first into (IV) and then into (II). I-CHCl<sub>3</sub>-sunlight or boiling NaOAc-EtOH has no effect on (III), but illumination in MeOH converts (IV) into (III) (~100%) or (V) into (VI). KOH-MeOH and light-CHCl<sub>3</sub>-I are without effect on (VI), as are KOH-MeOH and HCl-MeOH (room temp.) on (V). R. S. C.

**Constituents of pyrethrum flowers. XV. Presence of the cumulated system in the pyrethrolone side-chain.** F. B. LaForge and F. Acree, jun. (*J. Org. Chem.*, 1942, 7, 416–418).—The structure

OH·CH—CO—CH<sub>2</sub>·CH·C·CHMe for pyrethrolone is confirmed by the similar behaviour of pyrethron and *α*-cyclohexyl-Δ<sup>8,9</sup>-pentadiene towards halogen addition and subsequent reduction and by their similar absorption spectra. H W.

**Behaviour of carbonyl bridge compounds with alkaline hydrogen peroxide.** C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1942, 64, 2439–2442).—“*cis*”-4 : 7-endo-Keto-2 : 3 : 5 : 6-tetraphenyl-4 : 7 : 3a : 7a-tetrahydroinden-1-one (I) with aq. H<sub>2</sub>O<sub>2</sub>-NaOH at <30° absorbs 4 O, giving a peroxide, softens ~80°, decomp. up to 200°, which with KI- or HBr-AcOH regenerates (I) but in



boiling AcOH gives the “*trans*”-isomeride (II), m.p. variable, 215° of (I) *cf.* A., 1937, II, 457). (II) does not give a peroxide. At 260–270° (II) loses CO and undergoes a 1 : 2 shift of Ph, giving 3 : 3 : 5 : 6-tetraphenylindan-1-one (III) (structure proved below). In other respects (I) and (II) react similarly: both add 1 MgMeI and show 1 active H, with KOH-EtOH give 2 : 3 : 5 : 6-tetraphenyl-4 : 7 : 3a : 7a-tetrahydroinden-1-one-7-carboxylic acid, and with MgPhBr give the same carbinol etc. 3 : 3 : 5 : 6-Tetraphenylindan-1 : 2-dione (IV) [prep. from (III) by SeO<sub>2</sub> (*cf. loc. cit.*)] gives a *quinoxaline* derivative and with H<sub>2</sub>O<sub>2</sub>-NaOH-H<sub>2</sub>O-EtOH gives 4 : 5-diphenyl-2-benzhydrylbenzoic acid (V) (61%), m.p. 258–259° (*Me ester*, m.p. 165°), which with CuCO<sub>3</sub> at 260–265° gives 3 : 4-diphenyl-1-benzhydrylbenzene [4-benzhydryl-*o*-terphenyl] (30%), m.p. 143° (also prepared from 3 : 4 : 1-C<sub>6</sub>H<sub>5</sub>Ph<sub>2</sub>·COPh and MgPhBr and subsequent reduction by Zn-AcOH), and *aa* : 4 : 5-tetraphenylphthalide (VI) (20%), m.p. 180° (also prepared from 2 : 4 : 5 : 1-CO<sub>2</sub>H·C<sub>6</sub>H<sub>5</sub>Ph<sub>2</sub>·COPh and MgPhBr). (VI) is unaffected by Br, AcCl, or CrO<sub>3</sub>, and with Zn-AcOH gives (V). 2 : 2-Dibromo-3 : 3 : 5 : 6-tetraphenylindanone with MgPhBr gives first the 2-Br<sub>1</sub>-compound and then (III). MgRBr and (III) give 1 : 3 : 3 : 5 : 6-pentaphenylindan-1-ol, m.p. 233–234° (decomp.) (dehydrated by boiling 2% H<sub>2</sub>SO<sub>4</sub>-AcOH to 1 : 1 : 3 : 5 : 6-pentaphenylindene, m.p. 227°), 1 : 1 : 5 : 6-tetraphenyl-3-methyl-, m.p. 180°, and -3-*a*-naphthyl-indene, m.p. 244°. MgPhBr and (IV) in Bu<sub>2</sub>O at 100° give 1 : 2 : 3 : 3 : 5 : 6-hexaphenylindane-1 : 2-diol, m.p. 159°. R. S. C.

**General method for synthesis of acenaphthenequinones.** Buu-Hoi and P. Cagniant (*Compt. rend.*, 1942, 214, 315–317).—Acenaphtheneone (I), NO·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub>, and aq. 10% Na<sub>2</sub>CO<sub>3</sub> in EtOH at >40° give *acenaphthenequinonedimethylaminoanil*, m.p. 200–202°, readily hydrolysed (dil. H<sub>2</sub>SO<sub>4</sub>) to the quinone. 2 : 1-C<sub>10</sub>H<sub>6</sub>Me·CH<sub>2</sub>Cl and aq. EtOH-KCN afford the nitrile, b.p. 155°/0.5 mm. m.p. 79°, and thence 2 : 1-C<sub>10</sub>H<sub>6</sub>Me·CH<sub>2</sub>·CO<sub>2</sub>H [*chloride* (II), b.p. 148–150°/0.5 mm.; *amide*, m.p. 178°]; (II) with AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> or PhNO<sub>2</sub> gives 1-methylacenaphthen-7-one, b.p. 158°/21 mm., m.p. 120° (*semicarbazone*, m.p. 213–215°), converted [as for (I)] into 1-methylacenaphthenequinone, m.p. 200° [8-dimethylaminoanil, m.p. 137° (III); *quinoxaline* from *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, m.p. 198°]. (III) is accompanied by a little of the corresponding *bismethylacenaphthylidene-dione*, m.p. 254° (*cf. Sircar et al.*, A., 1933, 505). 4 : 1-C<sub>10</sub>H<sub>6</sub>Me·CH<sub>2</sub>Cl, b.p. 124–126°/2.1 mm., similarly yields 4-methyl-1-naphthylacetic acid, m.p. 148° [nitrile, b.p. 154–156°/0.5 mm.; *chloride*, b.p. 148°/0.5 mm., cyclised less readily than (II); *amide*, m.p. 209°], 3-methylacenaphthen-7-one, m.p. 92° [*semicarbazone*, m.p. 240° (decomp.)], and 3-methylacenaphthenequinone, m.p. 178° (8-dimethylaminoanil, m.p. 189°; *quinoxaline*, m.p. 262–263°). J. E. P.

**1-Nitro-5-aminoanthraquinone.**—See B., 1943, II, 45.

#### IV.—STEROLS AND STEROID SAPOGENINS.

**Sterols of alfalfa [lucerne] seed oil. II. Isolation of β- and δ-spinasterol.** I. C. King and C. D. Ball (*J. Amer. Chem. Soc.*, 1942, 64, 2488–2492; *cf. A.*, 1940, III, 83).—This oil yields sterols, giving

insol. acetates, which by hydrolysis and then fractionation by 85% EtOH yield *α*- (I), m.p. 168.5–169°, [α]<sub>D</sub><sup>25</sup> –2.7° (acetate, m.p. 180–182°, [α]<sub>D</sub><sup>25</sup> –6.4°; benzoate, m.p. 196–199°, [α]<sub>D</sub><sup>19</sup> +2.1°), and β-spinasterol, +0.5H<sub>2</sub>O, m.p. 148–150° (H<sub>2</sub>O lost at 110–125°), [α]<sub>D</sub><sup>20</sup> +5.9°, and anhyd., m.p. 148–150° [digitonide; *acetate* (II), m.p. 153–155°, [α]<sub>D</sub><sup>19</sup> +5.1°; *benzoate*, m.p. 181–183°, [α]<sub>D</sub><sup>19</sup> +7.5°]. The sol. acetates yield δ-spinasterol, +0.5H<sub>2</sub>O, m.p. 143–144°, [α]<sub>D</sub><sup>19</sup> +6.2° [digitonide; *acetate* (III), m.p. 132–133.5°, [α]<sub>D</sub><sup>16</sup> +0.8°; *benzoate*, m.p. 165–168°, [α]<sub>D</sub><sup>19</sup> +11.1°]. [α] are in CHCl<sub>3</sub>. Hydrogenation of (II) or (III) gives *α*-stigmasteryl acetate. Bessisterol (IV) (Kuwada *et al.*, A., 1941, II, 321) differs from (I) in [α]. The formulæ of Fernholz *et al.* (A., 1940, II, 373) for (I) may apply to (IV). R. S. C.

**Epimeric 7-hydroxycholesterols.** O. Wintersteiner and W. L. Ruigh (*J. Amer. Chem. Soc.*, 1942, 64, 2453–2457).—7-Ketocholesteryl acetate with Al(OPr<sup>i</sup>)<sub>3</sub>-Pr<sup>i</sup>OH and later 2% KOH gives crude 7(*α*)-hydroxycholesterol (I), m.p. ~176° (Windaus *et al.*, A., 1935, 1363), *di*-Δ<sup>4,6</sup>-cholestadien-3-yl or -Δ<sup>3,5</sup>-cholestadien-7-yl ether, m.p. 158–160°, [α]<sub>D</sub> +90.6° in CHCl<sub>3</sub> (absorption max. at 243 mμ., ε 54,000 in Et<sub>2</sub>O), and Δ<sup>4,6</sup>-cholestadien-3-one. (I) contains up to 20% of 7(*β*)-hydroxycholesterol, m.p. (+MeOH) 186° or (solvent-free) 154–157°, [α]<sub>D</sub><sup>23</sup> (+MeOH) –87.6° in CHCl<sub>3</sub>. Partial hydrolysis of the 3 : 7(*β*)-, m.p. 151–152.5° (lit. 155–157°), [α]<sub>D</sub><sup>23</sup> –107.5° in CHCl<sub>3</sub>, or 3 : 7(*α*)-dibenzoate gives the 7-mono-benzoates. The 3 : 7(*α*)-diacetate, m.p. 106–107°, [α]<sub>D</sub><sup>27</sup> +51.8° in CHCl<sub>3</sub>, and 7(*β*)-benzoate (II), m.p. 145–146°, [α]<sub>D</sub><sup>26</sup> –201° in CHCl<sub>3</sub>, (3 : 5-dinitrobenzoate, m.p. 178.5–179.5°, [α]<sub>D</sub><sup>23</sup> –88.2° in CHCl<sub>3</sub>; *H succinate*, m.p. 150–151°), are prepared. Pyrolysis of (II) gives little 7-dehydrosterol. R. S. C.

**Cholesteryl oxides.** P. N. Chakravorty and R. H. Levin (*J. Amer. Chem. Soc.*, 1942, 64, 2317–2322).—Cholesteryl acetate and *o*-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H in boiling Et<sub>2</sub>O give the β- (I) (58%), m.p. 111–112°, [α]<sub>D</sub><sup>25</sup> –21.8°, and *α*-oxide (II) (15%), new m.p. 101–103°, [α]<sub>D</sub><sup>25</sup> –44.6°. Cholesteryl benzoate gives only (50%) its *α*-oxide (III), m.p. 164–166°, [α]<sub>D</sub><sup>25</sup> –28.0°. Cholesterol gives its *α*- (IV) (61%), m.p. 141–143°, [α]<sub>D</sub><sup>25</sup> –44.5° [also obtained from (II) by KOH-MeOH], and a small amount of β-oxide (V), m.p. 105–107°, [α]<sub>D</sub><sup>25</sup> –12.7° [also obtained from (I)]. NH<sub>2</sub>·CO·NH·NH<sub>2</sub>·HCl and (I) in C<sub>5</sub>H<sub>5</sub>N at 100° give 6-chloro-5-hydroxy-3-acetoxycholestane (VI), m.p. 187.5–189.5°, unchanged by Ac<sub>2</sub>O and also obtained from (I) by boiling FeCl<sub>3</sub>-EtOH, BzCl-CCl<sub>4</sub>, or BzCl-C<sub>5</sub>H<sub>5</sub>N at room temp. and then 100°, or C<sub>5</sub>H<sub>5</sub>N·HCl in boiling EtOH. C<sub>5</sub>H<sub>5</sub>N·HCl in EtOH converts (III) into 6-chloro-5-hydroxy-3-benzoyloxycholestane (VII), m.p. 196–198° (unchanged by Ac<sub>2</sub>O), (II) into (VI), and (IV) or (V) into unstable Cl-compounds which are characterised by conversion into (VII) but which in MeOH-COMe<sub>2</sub> yield a halogen-free compound, m.p. 99–105°. BzCl with (II) gives a product, m.p. 160–170°, converted by Ac<sub>2</sub>O into (VI), with (III) or (IV) gives (VII), and with (V) gives (VII) and another substance, m.p. 197–198°. With boiling Na<sub>2</sub>CO<sub>3</sub>-EtOH-H<sub>2</sub>O, (VI) gives (IV), which is also obtained from (VII) by KOH-MeOH. The stereochemistry of the reactions is briefly discussed. R. S. C.

#### V.—TERPENES AND TRITERPENOID SAPOGENINS.

**Strophanthin.** E. Rabald and J. Kraus (*Z. physiol. Chem.*, 1940, 265, 39–51).—Reduction of strophanthidin (I) by Al-Hg or Al(OPr<sup>i</sup>)<sub>3</sub> gives strophanthinol (II), m.p. ~180° (softens at 150°) and m.p. 222–223° (corr.) after resolidifying at 180–190°, [α]<sub>D</sub><sup>12</sup> +37.1° in MeOH [*diacetate*, m.p. 193–195° (corr.)]. (II) cannot be hydrogenated completely in presence of Pd-black and with Pd-C or PdO absorbs 1 H<sub>2</sub> with formation of a product, m.p. 180–185°, and, if PdO is used, a substance, m.p. 205–206° (corr.) after melting and resolidifying at ~190°; in presence of PtO<sub>2</sub> (II) affords dihydrostrophanthinol, melts incompletely at 170–180°, resolidifies and melts at 207–208° (corr.), [α]<sub>D</sub><sup>15</sup> +35.5° in MeOH, identical with the compound obtained similarly from (I). *K*-Strophanthin-γ hepta-acetate is reduced [Al-Hg or Al(OPr<sup>i</sup>)<sub>3</sub>] to *K*-strophanthol-γ hepta-acetate, m.p. 172–173° (corr.), [α]<sub>D</sub><sup>21</sup> –84° in C<sub>6</sub>H<sub>6</sub>, hydrolysed by Ba(OMe)<sub>2</sub> in MeOH to *K*-strophanthol-γ (III), softens at 190°, decomp. 195–200°, [α]<sub>D</sub><sup>14</sup> +8.6° in MeOH [*octa-acetate* (IV), softens at 148°, m.p. 153–155° (corr.), [α]<sub>D</sub><sup>17</sup> +7.1° in C<sub>6</sub>H<sub>6</sub>], (III) is hydrolysed by acid to (II) and strophanthotriose, m.p. 225° (corr.; decomp.), [α]<sub>D</sub> +7.34° in H<sub>2</sub>O. Ba(OMe)<sub>2</sub>-MeOH and (IV) yield *K*-strophanthol-γ 18-acetate, m.p. 190–195° (decomp.), [α]<sub>D</sub><sup>14</sup> +9.85° in MeOH, which is hydrolysed to an acetylated genin. The nomenclature *K*-strophanthin-*α*, -*β*, and -*γ* is suggested for strophanthidin-cymarose (cymarol), strophanthidin-cymarose-glucose, and strophanthidin-cymarose-glucose-glucose respectively. H. W.

**Sapogenins. XVII. Position of the carboxyl group in oleanolic and glycyrrhetic acids.** G. A. R. Kon and W. C. J. Ross (*J.C.S.*, 1942, 741–744).—Me acetyldehydro-oleanolate (I) with SeO<sub>2</sub> in boiling AcOH gives a diketodehydro-ester (II), C<sub>33</sub>H<sub>46</sub>O<sub>6</sub>, m.p. 247–248°. [α]<sub>D</sub> –144° in CHCl<sub>3</sub> (*cf. Ruzicka et al.*, A., 1939, II, 331) which is saponified to a neutral substance (III), m.p. 286–289°, [α]<sub>D</sub> +204° in C<sub>5</sub>H<sub>5</sub>N (*cf. Jacobs et al.*, A., 1932, 749), and an acid,

m.p. 262—264°, which forms a *pyridazine* derivative, m.p. 263—265°. Oxidation ( $\text{H}_2\text{CrO}_4$ ) of (III) yields a *triketone*,  $\text{C}_{19}\text{H}_{40}\text{O}_3$ , m.p. >300° (decomp.). Acetyldeoxoglycyrrhetic ester (IV) similarly gives a *diketo-dehydro-ester*, m.p. 236—237°, isomeric with (II), and is hydrolysed to the *acid*, m.p. 248—249°,  $[\alpha]_D -39^\circ$  in  $\text{CHCl}_3$ , converted into the same hydroxy-diketone. Bromination of Me acetylglycyrrhetate affords a *Br<sub>2</sub>-ester*, decomp. 215—220°,  $[\alpha]_D +521^\circ$  in  $\text{CHCl}_3$ , and a *dehydro-ester*, m.p. 241—242°,  $[\alpha]_D +321^\circ$  in  $\text{CHCl}_3$ , which is reduced ( $\text{Zn-Hg-AcOH}$ ) to an *ester*,  $\text{C}_{33}\text{H}_{52}\text{O}_4$ , m.p. 258—259°,  $[\alpha]_D +127^\circ$  in  $\text{CHCl}_3$ . (I) and (IV) are therefore  $\beta$ -ketonic esters and support is thus afforded to the formulæ assigned to the parent acids (Bilham *et al.*, A., 1942, II, 418). F. R. S.

## VI.—HETEROCYCLIC.

**Analogues of synthetic tetrahydrocannabinol.** G. A. Alles, R. N. Icke, and G. A. Feigen (*J. Amer. Chem. Soc.*, 1942, **64**, 2031—2035).—*m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  (I) and  $\text{MgBu}^\alpha\text{Cl}$  in  $\text{Et}_2\text{O}$  give *α*-*m*-anisyl-*n*-amyl alcohol (92%), b.p. 128.5—129°/5 mm., dehydrated by  $\text{KHSO}_4$  at 135—160° to *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHPr}^\alpha$ , b.p. 92—99°/1 mm., which with  $\text{H}_2$ -PdO in EtOH at 3 atm. gives *m*-*n*-amylanisole (II) (81.5%), b.p. 97—98°/3 mm. *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$  [prep. from (I) by  $\text{H}_2$ -Raney Ni at 90°/90 atm.] with conc.  $\text{HCl-CaCl}_2$  gives the chloride, b.p. 75°/2 mm., which with  $\text{MgBu}^\alpha\text{Cl}$  gives (II). 30% aq.  $\text{HBr-AcOH}$  at 100° converts (II) into *m*-*n*-amylphenol, b.p. 99—100°/1 mm. (3 : 5-dinitrobenzoate, m.p. 70°), condensation of which with Et cyclohexanone-2-carboxylate (III) by  $\text{H}_2\text{SO}_4$  at <25° gives 5''-*n*-amyl-3' : 4' : 5' : 6'-tetrahydrodibenz-2-pyrone, b.p. 180—185° (bath)/10 μ., and thence ( $\text{MgMeI}$  in  $\text{PhOMe}$  at 100°) 2 : 2-dimethyl-5''-*n*-amyl-3' : 4' : 5' : 6'-tetrahydrodibenzpyran (99%), b.p. 140—145° (bath)/0.5 μ. Similarly are prepared 4'-methyl-5''-*n*-amyl-, 5''-methyl-, and 4' : 5''-dimethyl-, m.p. 105—106°, -3' : 4' : 5' : 6'-tetrahydrodibenz-2-pyrone, 2 : 2 : 4'-trimethyl-5''-*n*-amyl-, b.p. 155—160° (bath)/2 μ., 2 : 2 : 5''-trimethyl-, and 2 : 2 : 4' : 5''-tetramethyl-3' : 4' : 5' : 6'-tetrahydrodibenzpyran. *m*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OBu}^\alpha$  and (III) in  $\text{POCl}_3\text{-C}_6\text{H}_6$  give 5''-*n*-butoxy-3' : 4' : 5' : 6'-tetrahydrodibenz-2-pyrone (65%), m.p. 87—88°, b.p. 240—243°/3 mm., also obtained from the 5''-hydroxypyrone by  $\text{Bu}^\alpha_2\text{SO}_4\text{-2N-NaOH}$  at 90—110° and converted by  $\text{MgMeI-PhOMe}$  at 100° into 2 : 2-dimethyl-5''-*n*-butoxy-3' : 4' : 5' : 6'-tetrahydrodibenzpyran, b.p. 133—134° (bath)/1 μ. 2 : 2 : 4'-Trimethyl-5''-*n*-butoxy-3' : 4' : 5' : 6'-tetrahydrodibenzpyran, b.p. 162—168°/5 μ., is prepared from the 5-hydroxypyrone by  $\text{Bu}^\alpha_2\text{SO}_4\text{-2N-NaOH}$  at 90—100°. 2 : 2-Di- and 2 : 2 : 4'-tri-methyl-5''-ethoxy-3' : 4' : 5' : 6'-tetrahydrodibenzpyran, liquids, are similarly prepared. ( $\text{PrCO}$ )<sub>2</sub>O and a drop of  $\text{H}_2\text{SO}_4$  convert the 5''-hydroxypyrans into 5''-*n*-butoxy-2 : 2-di- and -2 : 2 : 4'-tri-methyl-3' : 4' : 5' : 6'-tetrahydrodibenzpyran, liquid; the corresponding 5''-acetoxypyrans, m.p. 65—66° and 59—60°, respectively, are prepared by  $\text{Ac}_2\text{O-C}_6\text{H}_5\text{N}$ . The above-named pyrans produce no ataxia in dogs (doses : 50—100 mg. per kg.) or corneal anæsthesia in rabbits (doses : 10—20 mg. per kg.) (cf. Ghosh *et al.*, A., 1941, II, 145). Synthetic tetrahydrocannabinol produces ataxia (8 mg. per kg.) but no corneal anæsthesia (doses up to 32 mg. per kg.) (cf. *loc. cit.*). R. S. C.

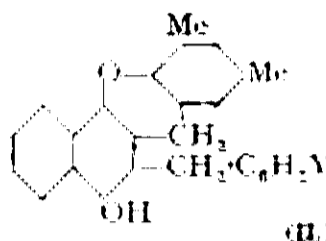
**Constitution of hibiscetin.** P. S. Rao (*Current Sci.*, 1942, **11**, 360; cf. A., 1942, II, 327).—2 : 4 : 3 : 6 : 1-(OH)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>·CO·CH<sub>2</sub>·OMe with [3 : 4 : 5 : 1-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>·CO]<sub>2</sub>O and (OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>·CO<sub>2</sub>Na gives 7-hydroxy-3 : 5 : 8 : 3' : 4' : 5'-hexa-, methylated to 3 : 5 : 7 : 8 : 3' : 4' : 5'-hepta-methoxyflavone (hibiscetin Me<sub>7</sub> ether). F. R. G.

**Products of the reaction of flavonols with boric acid and organic acids and its significance for the anchoring of boron in plant organs.** K. Tauböck (*Naturwiss.*, 1942, **30**, 439).—Evaporation of solutions or suspensions of flavonols (I),  $\text{H}_3\text{BO}_3$ , and  $\text{H}_2\text{C}_2\text{O}_4$  in  $\text{COMe}_2$  gives an  $\text{Et}_2\text{O}$ -sol., intensely yellow pigment (II) with marked yellow-green fluorescence very suitable for the detection and determination of traces of (I). (II) is not very stable and on repeated evaporation passes into an  $\text{Et}_2\text{O}$ -insol., non-fluorescent pigment similar to that obtained with citric and other acids; in dry  $\text{Et}_2\text{O}$  it can be kept for several hr. The most suitable mol. proportions are (I) :  $\text{H}_3\text{BO}_3$  :  $\text{H}_2\text{C}_2\text{O}_4$  = 1 : 1 : 4.  $\text{H}_2\text{C}_2\text{O}_4$  can be replaced by  $\text{CH}_2(\text{CO}_2\text{H})_2$  but succinic, fumaric, and adipic acid etc. are unsuitable. The presence of OH increases the reactivity. Polybasic CO-acids are unsuitable. Monobasic  $\text{NH}_2$ -acids give non-fluorescent,  $\text{Et}_2\text{O}$ -insol. pigments but dibasic  $\text{NH}_2$ -acids give some (II). Naringenin, campherol, quercetin, morin, quercetagenin, myricetin and its hexaacetate show the reaction, which is not exhibited by genistein, daidzein, flavone, or hesperitin. Anthocyanins and anthocyanidins give intensely coloured but non-fluorescent substances; this is true also of *l*-catechin, *dl*-epicatechin, curcumin, and phloretin. Evidence is adduced in favour of the view that B is partly immobilised in many plant organs by combination with (I). H. W.

**Optically active tetrahydrocannabinols.** XIV. *d*- and *l*-3''-Hydroxy-2 : 2 : 4'-trimethyl-5''-*n*-amyl-3' : 4' : 5' : 6'-tetrahydrodibenzpyran. R. Adam, C. M. Smith, and S. Loewe (*J. Amer. Chem. Soc.*, 1942, **64**, 2087—2089; cf. A., 1942, II, 236).—*dl*- is resolved by *l*-menth-hydrazide in EtOH, giving *l*-3-methylcyclohexanone, b.p. 164—168° (semicarbazone, m.p. 181°,  $[\alpha]_D^{25} +20.8^\circ$  in EtOH; *l*-menth-hydraz-

one, m.p. 146°,  $[\alpha]_D^{25} -31.3^\circ$  in EtOH). This and the *d*-ketone (prep. from pulegone; *l*-menth-hydrazide, softens at 126—130°, m.p. 130—136°) with  $\text{Et}_2\text{C}_2\text{O}_4\text{-NaOEt}$  at 3—5° (later room temp.) give *Et d*- and *l*-5-methylcyclohexanone-2-carboxylate, b.p. 122—124°/15 mm.,  $[\alpha]_D^{20} +90.5^\circ$  ( $\rightarrow +73^\circ$  by keto-enol equilibration),  $-84.6^\circ$ , and thence *d*- and *l*-3''-hydroxy-4'-methyl-5''-*n*-amyl-3' : 4' : 5' : 6'-tetrahydrodibenz-2-pyrone, m.p. 177°,  $[\alpha]_D^{25} +137^\circ$  in  $\text{CHCl}_3$ ,  $[\alpha]_D^{27} +133^\circ$ ,  $-127^\circ$  in EtOH, and *d*- and *l*-3''-hydroxy-2 : 2 : 4'-trimethyl-5''-*n*-amyl-3' : 4' : 5' : 6'-tetrahydrodibenzpyran, b.p. 175—185°/0.1 mm.,  $[\alpha]_D^{25} +147.5^\circ$  in  $\text{CHCl}_3$ ,  $+147^\circ$  in EtOH,  $[\alpha]_D^{26} -114^\circ$  in EtOH. The *d*- and *l*-pyrans are 0.38 and 1.66 times, respectively, as potent (by ataxia) as the *dl*-compound (cf. Leaf *et al.*, A., 1942, II, 202). R. S. C.

**Condensation of 1 : 4-dihydroxy-2-methylnaphthalene with formaldehyde and xylene alcohol.** H. von Euler and S. von Kispeszky (*J. pr. Chem.*, 1942, [ii], **180**, 195—202).—2 : 1 : 4- $\text{C}_{10}\text{H}_5\text{Me}(\text{OH})_2$  (I) (1 mol.),  $\text{CH}_2\text{O}$  (1.1 mols.), and  $\text{NaOH}$  (2 mols. as 10% solution) (room temp.; 48 hr.) yield a yellow compound,  $\text{C}_{23}\text{H}_{16}\text{O}_4$  (probably 3-methylenebis-2-methylnaphthaquinone), and colourless material. (I) (1 mol.),  $\text{CH}_2\text{O}$  (1.1 mol.), and conc.  $\text{HCl}$  (0.1 mol.) afford a product, m.p. 280°, which with  $\text{Ac}_2\text{O-C}_6\text{H}_5\text{N}$  (100°; 2 hr.) yields



a compound,  $\text{C}_{23}\text{H}_{22}\text{O}_6$ , m.p. 305—306° (probably di-*l*-acetoxy-2-methylnaphtha-pyran), and a compound,  $\text{C}_{31}\text{H}_{28}\text{O}_8$ , m.p. 238° (probably 3-methylenebis-1 : 4-di-acetoxy-2-methylnaphthalene). *m*-4-Xylene (1 mol.), (I) (2.5 mols.), and 96%  $\text{HCl-EtOH}$  (15 min.; 100°) yield a compound,  $\text{C}_{28}\text{H}_{26}\text{O}_8$ , m.p. 204° [probably (II)] (acetate, m.p. 230—231°). W. C. J. R.

**Thionaphthen-indigotins.**—See B., 1943, II, 47.

**Phenoxthionins.**—See B., 1943, II, 45.

**Reaction products from α-chloroketones and potassium cyanide.** III. **Cyanoacetylacetone and a new method of preparing acetylacetone.** R. Justoni (*Gazzetta*, 1941, **71**, 375—388).—5-Hydroxy-2 : 4-dicyano-2 : 5-dimethyltetrahydrofuran (I) (A., 1942, II, 326) with aq.  $\text{NaOH}$  gives  $\alpha$ -cyanoacetylacetone cyanohydrin,  $\text{COMe}\cdot\text{CH}(\text{CN})\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CN}$ , a syrup, which when distilled gives  $\alpha$ -cyanoacetylacetone (II) (*loc. cit.*) ( $\text{FeCl}_3$  reaction; *Cu* salt), from which it is also obtained by action of  $\text{HCN}$  and  $\text{KOH}$ . With boiling conc.  $\text{HCl}$ , (II) gives 3-cyano-2 : 5-dimethylfuran (III), b.p. 183—183.5°, hydrolysed by 20%  $\text{KOH}$  in aq. EtOH to the amide, m.p. 125°, of 2 : 5-dimethylfuran-3-carboxylic acid. With boiling aq.  $\text{NH}_3$  (or solid  $\text{NH}_4$  carbonate, or  $\text{NH}_4\text{OAc-AcOH}$ ), (II) gives 3-cyano-2 : 5-dimethylpyrrole, m.p. 89—90° (also obtained from  $\text{COMe}\cdot\text{CHNa}\cdot\text{CN}$ ,  $\text{CH}_2\text{Cl}\cdot\text{COMe}$ , and aq.  $\text{NH}_3$ ), which with 50% aq.  $\text{KOH}$  gives the amide, m.p. 160—161°, of 2 : 5-dimethylpyrrole-3-carboxylic acid. With  $\text{P}_2\text{S}_3$  or  $\text{P}_2\text{S}_5$  at 85—90°, (II) gives (III) and some 3-cyano-2 : 5-dimethylthiophen, b.p. 225—233° (decomp.) (also obtained from 2 : 5-dimethylthiophen and  $\text{BrCN-AlCl}_3$ ), which is hydrolysed to the corresponding amide. At 70°, (I) and dil.  $\text{H}_2\text{SO}_4$  give  $\gamma$ -cyano- $\alpha$ -aceto- $\gamma$ -valerolactone (IV) (cf. Obregia, A., 1892, 324), which in aq.  $\text{NaOH}$  gives acetylacetone [50% yield from (I)]. With  $\text{RN}_2\text{Cl}$ , (IV) gives the phenylhydrazone (V), m.p. 208°, and *p*-nitrophenylhydrazone (VI), m.p. 227°, of  $\gamma$ -cyano- $\alpha$ -keto- $\gamma$ -valerolactone. (Similarly  $\alpha$ -aceto- $\beta$ -ethylidenepropio- $\gamma$ -lactone gives the corresponding  $\alpha$ -phenylhydrazone.) With  $\text{EtOH-HCl}$ , (V) gives  $\alpha$ -keto- $\gamma$ -carbethoxy- $\gamma$ -valerolactone phenylhydrazone. With boiling 5%  $\text{NaOH}$ , (V) gives 1-phenyl-5-methylpyrazole-3-carboxylic acid. Similarly (VI) gives 1-*p*-nitrophenyl-5-methylpyrazole-3-carboxylic acid, new m.p. 219—220° (decomp.), of which the *Me* ester, m.p. 174—175°, is obtained from  $\text{COMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Me}$  and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ . E. W. W.

**Nicotin-*p*-phenetide.**—See B., 1943, III, 41.

4- $\delta$ -Diethylaminoamylamino-6-methoxy-, b.p. 210—212°/1.5—2 mm., 5 : 6 : 7-trimethoxy-2-methyl-, b.p. 142°/2 mm. (8-nitro-, m.p. 115°, and 8-amino-derivative, b.p. 153°/2 mm.), and 8- $\gamma$ -dimethylaminobutylamino-6-hydroxy-quinoline, m.p. 118° (*O*-acetyl derivative, b.p. 195—200°/1 mm.).—See A., 1943, III, 136.

**Synthetic application of  $\alpha$ - $\beta$ -bromoethylbenzyl bromide.** I. **Sulphanilamide derivatives of 1 : 2 : 3 : 4-tetrahydroisoquinoline.** F. G. Holliman and F. G. Mann (*J.C.S.*, 1942, 737—741).—The prep. of *o*- $\text{Br}\cdot[\text{CH}_2]_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br}$  (I) is improved by treating *o*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}_2\text{Br}$  with  $\text{NaOEt}$  to give *o*-bromobenzyl *Et* ether, b.p. 119—120°/18 mm., which under special conditions with  $\text{EtBr}$  undergoes the Grignard reaction in combination with  $(\text{CH}_2)_2\text{O}$  to form *o*- $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OEt}$ , converted by  $\text{HBr-AcOH}$  into (I). *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$  and (I) with  $\text{K}_2\text{CO}_3$  yield 2-*p*-toluenesulphonyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, m.p. 142°. Similarly, (I) and *p*- $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$  give 2-*p*-acetamidobenzenesulphonyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, m.p. 175—176°, hydrolysed ( $\text{HCl}$ ) to the  $\text{NH}_2$ -compound, m.p. 174°, also obtained by direct condensation, along with 2-[*p*-(2'-1' : 2' : 3' : 4'-tetrahydroisoquinolyl)-benzenesulphonyl]-1 : 2 : 3 : 4-tetrahydroisoquinoline, m.p. 157—157.5°.

$p$ -NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Na, Na<sub>2</sub>CO<sub>3</sub>, and (I) afford, after acidification,  $p$ -[2:1:2:3:4-tetrahydroisoquinolyl]benzenesulphonic acid (+0.5H<sub>2</sub>O), m.p. 236–237 (efferv.), which with PCl<sub>5</sub>·NH<sub>3</sub> gives in small yield the -sulphonamide, m.p. 163°, remelts 182–184°. 1-Amino-1:2:3:4-tetrahydroquinoline sulphate and  $p$ -NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Cl with NaOH form  $p$ -acetamidobenzenesulphon-1-(1:2:3:4-tetrahydroquinolyl)-amide, m.p. 203° (decomp.), which could not be hydrolysed.  $p$ -NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH·NH<sub>2</sub> and  $p$ -NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Cl in C<sub>6</sub>H<sub>5</sub>N give  $s$ -di- $p$ -acetamidobenzenesulphonhydrazide, m.p. >300°, hydrolysed (HCl) to the NH<sub>2</sub>-compound (+H<sub>2</sub>O), m.p. 203° (decomp.). The bactericidal properties of the compounds are recorded. F. R. S.

**Quinoline derivatives of sulphanilamide.** O. G. Backeberg and J. L. C. Marais (*J.C.S.*, 1942, 758).—By condensing sulphanilamide with the appropriate chloro-lepidine and -quinaldine derivatives in AcOH, the following have been prepared: N<sup>4</sup>-(2'-lepidyl)-, m.p. 258°, N<sup>4</sup>-(6'-methoxy-, m.p. 249°, and N<sup>4</sup>-(6'-ethoxy-2'-lepidyl)-, m.p. 278°; N<sup>4</sup>-(4'-quinaldyl)-, m.p. 280° (decomp.); N<sup>4</sup>-(6'-methoxy-, m.p. 301° (decomp.), -(8'-methoxy-, m.p. 293° (decomp.), -(6'-ethoxy-, m.p. 308° (decomp.), and -(8'-ethoxy-4'-quinaldyl)-sulphanilamide, m.p. 277° (decomp.). F. R. S.

**New synthesis of heterocyclic compounds. I. 2:3-Dialkyl-quinolines.** V. A. Petrow (*J.C.S.*, 1942, 693–696).—By treating the anil, R·CO·CHR·CH·NAr, prepared by condensing equiv. amounts of CHO·CHMe·COMe or formylcyclohexanone and the appropriate amine in EtOH, with the amine hydrochloride and ZnCl<sub>2</sub> in EtOH, the following have been obtained: 2:3-dimethyl-5:6-benzoquinoline, m.p. 124–125° [picrate, m.p. 260–261° (decomp.)], from  $\gamma$ -( $\beta'$ -naphthyl-, m.p. 171–172°, and  $\gamma$ -( $\alpha'$ -naphthyl-iminomethyl)-butan- $\beta$ -one, m.p. 110–111°; 6:7:8:9-tetrahydro-1:2-benzacridine, m.p. 96.5–97.5° [picrate, m.p. 210.5–211.5° (decomp.)], from 1-( $\alpha$ -naphthyliminomethyl)cyclohexan-2-one, m.p. 118–119°; 1-( $\beta$ -naphthyliminomethyl)cyclohexan-2-one, m.p. 181–182°; 9-, m.p. 77–78° [picrate, m.p. 215–216° (decomp.)], and 8-methyl-1:2:3:4-tetrahydroacridine, m.p. 100–101° [picrate, m.p. 189–190° (decomp.)], prepared from 1-( $m$ -tolyliminomethyl)cyclohexan-2-one, m.p. 152–153°, and dehydrogenated to 2-methylacridine, m.p. 129–130° (lit. 125–126°) [picrate, m.p. 225–226° (decomp.)]; 7-methyl-1:2:3:4-tetrahydroacridine, m.p. 61–62° [picrate, m.p. 189.5–190.5° (decomp.)], prepared from 1-( $p$ -tolyliminomethyl)cyclohexan-2-one, m.p. 163–164°; picrate, m.p. 184–185° (decomp.), of 2-methyl-1:2:3:4-tetrahydroacridine; 1-anilomethyl-4-methylcyclohexan-2-one, m.p. 161–162°; 6:9-dimethyl-1:2:3:4-tetrahydroacridine, m.p. 38–39° [picrate, m.p. 187–188° (decomp.)], from 1-( $p$ -xylyliminomethyl)cyclohexan-2-one, m.p. 100–101°; 7-phenyl-1:2:3:4-tetrahydroacridine, m.p. 130° [picrate, m.p. 246–247° (decomp.)], from 1-(diphenyl-4'-iminomethyl)cyclohexan-2-one, m.p. 201–202°, and dehydrogenated to 3-phenylacridine, m.p. 127–128° [picrate, m.p. 244–245° (decomp.)]; 9-, m.p. 94.5–95.5° [picrate, m.p. 197–198° (decomp.)], and 6(or 8)-chloro-1:2:3:4-tetrahydroacridine, m.p. 92° [picrate, m.p. 204–205° (decomp.)], from 1-( $m$ -chloroanilomethyl)cyclohexan-2-one, m.p. 148–150°; 7-chloro-1:2:3:4-tetrahydroacridine, m.p. 95–96° [picrate, m.p. 188–189° (decomp.)], from 1-( $p$ -chloroanilomethyl)cyclohexan-2-one, m.p. 169–170°; 9-, m.p. 79–80° [picrate, m.p. 191–192° (decomp.)], and 6(or 8)-bromo-1:2:3:4-tetrahydroacridine, m.p. 86–87° [picrate, m.p. 213.5–214.5° (decomp.)], from 1-( $m$ -bromoanilomethyl)cyclohexan-2-one, m.p. 155–156°; 1-( $p$ -bromoanilomethyl)cyclohexan-2-one, m.p. 175–176°; 7-iodo-1:2:3:4-tetrahydroacridine, m.p. 86.5–87.5° [picrate, m.p. 219.5–220.8° (decomp.)], from 1-( $p$ -iodoanilomethyl)cyclohexan-2-one, m.p. 168–169°; 6(or 8)-carbethoxy-1:2:3:4-tetrahydroacridine, m.p. 63–64° [picrate, m.p. 161° (decomp.)], from 1-( $m$ -carbethoxyanilomethyl)cyclohexan-2-one, m.p. 143–144°; 7-carbethoxy-1:2:3:4-tetrahydroacridine, m.p. 94.5–95.5° [picrate, m.p. 197–198° (decomp.)], from 1-( $p$ -carbethoxyanilomethyl)cyclohexan-2-one, m.p. 181–182°, and hydrolysed to 1:2:3:4-tetrahydroacridine-7-carboxylic acid, m.p. 290–291°; 1-( $o$ -carboxy-, m.p. 199–200°, and 1-( $o$ -carbo-methoxy-anilomethyl)cyclohexan-2-one, m.p. 134.5–135.5°, which do not give acridine derivatives; 7-hydroxy-1:2:3:4-tetrahydroacridine, m.p. 290–291° [picrate, m.p. 229.5–230.5° (decomp.)], from 1-( $p$ -hydroxyanilomethyl)cyclohexan-2-one, m.p. 154–155°; 7-nitro-, m.p. 170.5–171.5° [picrate, m.p. 204.5° (decomp.)], from 1-( $p$ -nitroanilomethyl)cyclohexan-2-one, m.p. 244–245°, reduced to 7-amino-1:2:3:4-tetrahydroacridine, m.p. 141° (Ac derivative, m.p. 218.5–219.5°); 1-( $m$ -nitroanilomethyl)cyclohexan-2-one, m.p. 171–172°, which does not form an acridine derivative; 9-methoxy-1:2:3:4-tetrahydroacridine, m.p. 121.5–122.5° [picrate, m.p. 206.5–207.5° (decomp.)], from 1-( $o$ -methoxyanilomethyl)cyclohexan-2-one, m.p. 131–132°; 7-methoxy-1:2:3:4-tetrahydroacridine, m.p. 90–91° [picrate, m.p. 223.5–224.5° (decomp.)], from 1-( $p$ -methoxyanilomethyl)cyclohexan-2-one, m.p. 149–150°; 6(or 8)-acetyl-1:2:3:4-tetrahydroacridine, m.p. 131–132° [picrate, m.p. 211–212° (decomp.)], from 1-( $m$ -acetylanilomethyl)cyclohexan-2-one, m.p. 139–140°; and 7-anilino-1:2:3:4-tetrahydroacridine, m.p. 173° [picrate, m.p. 251–252° (decomp.)], from 1-( $p$ -anilinoanilomethyl)cyclohexan-2-one, m.p. 144–145°. A mechanism for the reaction is suggested. F. R. S.

**Sulphanilamide derivatives of histidine.** M. Amorosa (*Gazzetta*, 1941, 71, 343–350).—Histidine hydrochloride in aq. NaOH with  $p$ -SO<sub>2</sub>Cl·C<sub>6</sub>H<sub>4</sub>·NHAc gives the N-Ac derivative (I), m.p. (+3H<sub>2</sub>O) 122–132°, (anhyd.) decomp. 242–243° (quinine salt, m.p. 135°), of  $p$ -aminobenzenesulphonylhistidine (II), m.p. 263–264° (decomp.) [ $p$ -carbamido-derivative, m.p. 229–231° (decomp.)]. With MeOH·HCl, (I) or (II) gives the Me ester dihydrochloride (III), m.p. 218–225° (decomp.), of (II). Diazotisation of (II) and (III) and coupling with  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH gives products, m.p. 255–257°, and 165–170°, respectively. E. W. W.

**N-Substituted barbituric acids.** J. S. Buck, W. S. Ide, and R. Baltzly (*J. Amer. Chem. Soc.*, 1942, 64, 2233).—1-Phenyl- yields 1- $p$ -nitrophenyl-, m.p. 188°, and thence 1- $p$ -aminophenyl-5-ethyl-5-isobutylbarbituric acid, m.p. 153°. The appropriate carbamides and malonic esters yields 1- $o$ -phenetyl-, m.p. 193.5°, 1- $p$ -ethylphenyl-5-ethyl-5- $n$ -butyl-, m.p. 107°, and 5:5-diethyl-1- $n$ -hexyl-, m.p. 41°, -barbituric acid. R. S. C.

**Barbituric acids.**—See B., 1943, III, 42.

**Lysine and ornithine.**—See A., 1943, II, 55.

**Convenient synthesis of *dl*-methionine.** H. R. Snyder, J. H. Andreen, G. W. Cannon, and C. F. Peters (*J. Amer. Chem. Soc.*, 1942, 64, 2082–2084).—Hydrogenation (Raney Ni) of  $\alpha$ -keto- $\gamma$ -butyrolactonephenylhydrazine in EtOH at 100–150°/1700 lb. gives 3:6-diketo-2:5-di- $\beta$ -hydroxyethylpiperazine (I) (54%), m.p. 178–180°, but in Ac<sub>2</sub>O at 125°/2000 lb. gives  $\alpha$ -acetamido- (30%), m.p. 82–84°, b.p. 175–178°, hydrolysed to  $\alpha$ -amino- $\gamma$ -butyrolactone (40%) (hydrochloride, m.p. 200–201°). H<sub>2</sub>-Pd-C in MeOH converts  $\alpha$ -oximino- $\gamma$ -butyrolactone (prep. by OEt·NO-MeOH), m.p. 183–185°, in MeOH into (I) (55–60%), m.p. 186° (decomp.). SOCl<sub>2</sub> at 0° to –5° (later warm) and (I) give 3:6-diketo-2:5-di- $\beta$ -chloroethylpiperazine, m.p. 230–231°, which with NaSMc (2.2 mols.) in EtOH gives 3:6-diketo-2:5-di- $\beta$ -methylthioethylpiperazine, m.p. 231–232°, converted by conc. HCl into *dl*-methionine (85–95%). R. S. C.

**Glyoxalines. II. Interaction of benzamidine with phenylglyoxal.** R. C. Waugh, J. B. Ekeley, and A. R. Ronzio (*J. Amer. Chem. Soc.*, 1942, 64, 2028–2031; cf. A., 1942, II, 379).—Data of Kunckell *et al.* (A., 1901, i, 758) are erroneous. Adding conc., aq. KOH to BzCHO·H<sub>2</sub>O (I) and NH<sub>2</sub>·CPh·NH in EtOH gives  $\alpha$ -hydroxyphenacylbenzamidine (II) (40%), OH·CHBz·NH·CPh·NH, +0.5EtOAc, m.p. 112–115° (decomp.). Adding a little 50% aq. KOH to (I) and NH<sub>2</sub>·CPh·NH<sub>2</sub>Cl (III) in warm H<sub>2</sub>O and then boiling gives 4-hydroxy-3:4-diphenylglyoxaline [? 5-keto-2:4-diphenyl-4:5-dihydroglyoxaline] (IV) (64%), +0.5 dioxan, m.p. 251–252° (acetate, m.p. 174°), also obtained by adding acid to (II) in hot alkali. In boiling AcOH, (I) and (III) give 4:5-dihydroxy-2:4-diphenyl-4:5-dihydroglyoxaline hydrochloride (62%), darkens at 260°, m.p. 282° (diacetate, m.p. 181°, of the free base), which is also obtained by adding an excess of conc. HCl to (II) or (IV) in alkali and in absence of acid rapidly gives (IV). In EtOH containing a trace of alkali, (IV) gives (?) a polymeride, darkens at 250°, m.p. 262°, whence it is regenerated by hot alkali. In aq. NaOAc at room temp., (I) and (III) give 4:5-dihydroxy-2:5-diphenyl-1- $\alpha$ -hydroxyphenacyl-4:5-dihydroglyoxaline (87%), m.p. 73–80°, which in EtOH yields (IV). In boiling H<sub>2</sub>O, (I) and (III) give NH<sub>3</sub> and a substance (<1%), C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>, m.p. 170–172°. Absorption spectra of the products are recorded. R. S. C.

**Pyrazole compounds. I. Reaction product of phenylhydrazine and ethyl cyanoacetate.** A. Weissberger and H. D. Porter (*J. Amer. Chem. Soc.*, 1942, 64, 2133–2136).—Contrary to Conrad *et al.* (A., 1906, i, 608), CN·CH<sub>2</sub>·CO<sub>2</sub>Et, NPh·NH<sub>2</sub>, and NaOEt (2 mols. essential) in EtOH give 3-amino-1-phenyl-5-pyrazolone (I) (43%), m.p. 218–220° {N-Bz, m.p. 220–221°, N-CO<sub>2</sub>Et- (II), m.p. 198–199°, (?) (CO<sub>2</sub>Et)<sub>2</sub>, m.p. 106–108° [with a little piperidine in boiling EtOH gives (II)]}, and N-NH<sub>2</sub>·CO-derivative, m.p. 235–236°. With AcCl in dioxan, (I) gives the 3-Ac derivative (III), m.p. 218–220°, but with boiling Ac<sub>2</sub>O gives the ON-Ac<sub>2</sub> derivative, m.p. 144–145°, hydrolysed to (III) by cold 2% NaOH. NPh·N:C(CO<sub>2</sub>Et)·CH<sub>2</sub>·CO<sub>2</sub>Et in boiling AcOH-C<sub>6</sub>H<sub>6</sub> gives Et 1-phenyl-5-pyrazolone-3-carboxylate (80%; less under other conditions), m.p. 185–186°, converted by 28% aq. NH<sub>3</sub> at room temp. into the amide (57%), m.p. 233–235° (decomp.), and by 42% aq. N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O at room temp. into the hydrazide (86%), m.p. 235–237° (decomp.). With HCl-aq. EtOH-NaNO<sub>2</sub> at 5° this gives the azide (62%), deflagrates at 140°, and thence (boiling EtOH) (II) and (10% NaOH at 100°) (I) (proof of structure). R. S. C.

**Pyrrole series. IX. Determination of the bridge structure of dipyrrolymethanes. Estimation of active hydrogen.** A. H. Corwin and R. C. Ellingson. **X. Rearrangements of pyrrole rings in the oxidation of dipyrrolymethanes.** A. H. Corwin and K. J. Brunings (*J. Amer. Chem. Soc.*, 1942, 64, 2098–2106, 2106–2115; cf. A., 1942, II, 380).—IX. NH in pyrroles (9 examples) and dipyrrolymethanes (12 examples) is determined by titration with NaCPh<sub>3</sub> in Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> or -dioxan-N<sub>2</sub>, the indicator being the colour of the reagent. Blanks on solvents are necessary. Technique and apparatus are

details: C-Substitution by Me, CO<sub>2</sub>Et, or Br does not interfere, but COMe consumes additional reagent. NaCPh<sub>3</sub> reacts with substances which are indifferent to molten Na or K. The reaction mechanism can be checked by hydrolysis to the starting material or conversion by Me<sub>2</sub>SO<sub>4</sub> into the N-Me compound; dimethylation is thus possible. 3:5-Dicarbethoxy-2:4-dimethylpyrrole thus gives the 1:2:4-Me<sub>3</sub> compound. 3:5:3':5'-Tetracarbethoxy-4:4'-dimethyldipyrrylmethane with 1 or 2 NaCPh<sub>3</sub> and then Me<sub>2</sub>SO<sub>4</sub> gives the 1:4:4'-Me<sub>3</sub> and 1:4:1':4'-Me<sub>4</sub> (I) compound, respectively. (I) gives a red Na salt (N-Na salts are colourless), in which the Na is probably in the bridge CH<sub>2</sub>, since the salt cannot be methylated and by hydrolysis regenerates (I). 4:4'-Dicarbethoxy-3:5:3':5'-tetramethyldipyrrylmethane with 2 NaCPh<sub>3</sub> and then Me<sub>2</sub>SO<sub>4</sub> gives the 1:3:5:1':3':5'-Me<sub>6</sub> compound (II); use of 1 mol. of NaCPh<sub>3</sub> gives a mixture of (II) and 1:3:5:3':5'-Me<sub>5</sub> compound, m.p. 176° (decomp.) [converted into (II) by further treatment]. 1 NaCPh<sub>3</sub> reacts with the more acidic NH of 4:3':5'-tricarbethoxy-3:5:4'-trimethyldipyrrylmethane, yielding with Me<sub>2</sub>SO<sub>4</sub> the 3:5:1':4'-Me<sub>4</sub> compound (III); when the Na<sub>2</sub> salt reacts with 1 mol. of Me<sub>2</sub>SO<sub>4</sub> the more basic NNa reacts, yielding the 1:3:5:4'-Me<sub>4</sub> compound, m.p. 97° [also obtained from 3:5-dicarbethoxy-4-methyl-2-chloromethylpyrrole and 3-carbethoxy-1:2:4-trimethylpyrrole (V) in boiling MeOH]; the Na<sub>2</sub> salt and 2 mols. of Me<sub>2</sub>SO<sub>4</sub> give the 1:3:5:1':4'-Me<sub>5</sub> compound (VI), m.p. 129°, also obtained from 3:5-dicarbethoxy-1:4-dimethyl-2-chloromethylpyrrole and (V) in boiling MeOH and from (IV) by NaCPh<sub>3</sub> and then Me<sub>2</sub>SO<sub>4</sub>. NaCPh<sub>3</sub> and (III) in dioxan give a blue-fluorescent, red, later violet, solution, whence H<sub>2</sub>O or Me<sub>2</sub>SO<sub>4</sub> yields a compound, C<sub>20</sub>H<sub>24</sub>O<sub>5</sub>N<sub>2</sub>, m.p. 203—204°, but in C<sub>6</sub>H<sub>6</sub> gives a colourless Na salt, which, as usual, with H<sub>2</sub>O regenerates (III) and with Me<sub>2</sub>SO<sub>4</sub> gives (VI).

X. 4:4'-Dicarbethoxy-1:3:5:3':5'-pentamethyldipyrrylmethane (VII) [prep. from 3-carbethoxy-2:4-dimethylpyrrole and (V) in CH<sub>2</sub>O-aq. MeOH at 45°], m.p. 178—179°, with 1 mol. of Br in CCl<sub>4</sub> gives HBr, 4:4'-dicarbethoxy-3:5:3':5'-tetramethyldipyrrylmethane (VIII) (58%), m.p. 189—190° (decomp.), and 4-carbethoxy-1:3:5-trimethylpyrrole (IX) and with 0.5 mol. of Br gives HBr, 96% of (VIII), and 4:4'-dicarbethoxy-1:3:5:1':3':5'-hexamethyldipyrrylmethane (X). (VIII) is also obtained from (VII) by HCO<sub>2</sub>H-HBr or Cl<sub>2</sub>-CCl<sub>4</sub>, but not by neutral or basic oxidising agents. (VIII) and (X) absorb Br equally rapidly, (VII) more slowly. Cl<sub>2</sub> is absorbed very rapidly by (VII), but pptn. of (VIII) is then slow. 3-Carbethoxy-2:4-dimethylpyrrole with aq. HBr and HCO<sub>2</sub>H at 65° (not room temp.) gives (VIII). Neutral KMnO<sub>4</sub> oxidises 4:4'-dicarbethoxy-3:5:3':5'-tetramethyldipyrrylmethane (XI), but not (VII), to (VIII). (VII) is unaffected by CH<sub>2</sub>O-HBr. Br converts (VII) and (X) into (VIII) (85.4%) and the 1:3:5:1':3':5'-Me<sub>6</sub>-methene. (VII) and (X) with HBr-CCl<sub>4</sub> give 95% of (VIII). 4:4':4''-Tricarbethoxy-1:3:5:3':5':3''-5'-heptamethyltripyrrylmethane and HBr-CCl<sub>4</sub> give (XI) (90%) and (V). 3:5-Dicarbethoxy-4-methyl-2-dichloromethylpyrrole and (VII) in dioxan-HCl give (VIII). Br-CCl<sub>4</sub> converts 4:3':5'-tricarbethoxy-3:5:4'-trimethyldipyrrylmethane into 4:3':5'-tricarbethoxy-3:5:4'-trimethyldipyrrylmethane (83%), m.p. 125° (decomp.), but converts 3:5:4'-tricarbethoxy-1:4:3':5'-tetramethyldipyrrylmethane into (VIII) [and, presumably, 2:4:2':4'-tetracarbethoxy-1:3:1':3'-tetramethyldipyrrylmethane (not isolated)]. "Disproportionation" of (VII) by Br is thus shown to be due to fission of C-CH<sub>2</sub> and not of NMe; reaction mechanisms involving 2-CHBr<sub>2</sub>- and 2-H monopyrrole derivatives are discussed.

R. S. C.

**Methoxyglucobilins, a new type of bilirubinoid pigment; Gmelin's reaction.** H. Fischer and H. Reinecke (*Z. physiol. Chem.*, 1940, **265**, 9—21).—Bilirubin is dehydrogenated by p-O-C<sub>6</sub>H<sub>4</sub>-O in AcOH to biliverdin, converted by FeCl<sub>3</sub> into the compound, C<sub>33</sub>H<sub>35</sub>O<sub>6</sub>N<sub>4</sub>Cl<sub>4</sub>Fe; this is converted by NaOH followed by AcOH and then by CH<sub>2</sub>N<sub>2</sub> into biliverdin Me<sub>2</sub> ester, m.p. 213°, which gives the compound, C<sub>35</sub>H<sub>39</sub>O<sub>6</sub>N<sub>4</sub>Cl<sub>4</sub>Fe, m.p. 257°. Formylneoxanthobilirubic acid is condensed with vinylneoxanthobilirubic acid (I) to Me<sub>2</sub> 1':8'-dihydroxy-1:3:6:8-tetramethyl-7-ethyl-2-vinyl-2'-α-4'-ms-bilitriene-4:5-dipropionate, m.p. 225° (corresponding ferrobilin, m.p. 262°). The ferrobilin, m.p. 262°, and Zn complex salt of Me<sub>2</sub> 1':8'-dihydroxy-1:3:6:7-tetramethyl-8-ethyl-2-vinyl-2'-α-4'-ms-bilitriene-4:5-dipropionate are described. (I) and 3:3'-dimethyl-5:5'-dibromomethylpyrrromethene-4:4'-dipropionic acid hydrobromide afford Me<sub>2</sub> 1':12'-dihydroxy-1:3:6:7:10:12-hexamethyl-2:11-divinylhexapyrrrene-4:5:8:9-tetrapropionate, m.p. 242°. The Zn complex salt is dehydrogenated to dimethoxyætioglucobilin, m.p. 193° (corresponding Cu complex). Glucobilin IX α-Me<sub>2</sub> ester affords a Zn complex C<sub>35</sub>H<sub>40</sub>O<sub>6</sub>N<sub>4</sub>Zn, m.p. 305°, converted into the dimethoxyglucobilin ester, C<sub>37</sub>H<sub>48</sub>O<sub>8</sub>R<sub>4</sub>, m.p. 160—162°. Glucobilin XIIIa gives a (OMe)<sub>2</sub>-compound, C<sub>37</sub>H<sub>48</sub>O<sub>8</sub>N<sub>4</sub> (Cu complex). Me 6'-bromo-1'-hydroxy- is converted into Me 1':6'-dihydroxy-2:3:6-trimethyl-1:5-diethyltripyrrene-4-propionate. It is shown that the violet stage of the Gmelin reaction is not explicable by the formation of dihydroxytripyrrenes.

H. W.

**Isomerisation of chlorophylls a and b.** H. H. Strain and W. M. Manning (*J. Biol. Chem.*, 1943, **146**, 275—276).—Chromatographic adsorption (dry powdered sugar; light petroleum) of plant extracts

shows that chlorophylls a (I) and b (II) are accompanied by small amounts of two other green pigments, chlorophylls a' (III) and b' (IV). The adsorption column is washed with light petroleum containing 0.5% of Pr<sup>o</sup>OH and 0.5% of NPhMe<sub>2</sub>; (III) forms the lowest green band, and (IV) separates between (I) and (II). Higher plants and green algæ extracted at or at > room temp. yield (III) and (IV), but only traces are obtained by extraction at -80°. Plants not containing (II) do not yield (IV). (I) and (III), and (II) and (IV), are interconvertible, rapidly in Pr<sup>o</sup>OH at 95—100°, to give equilibrium mixtures containing 20% of the new isomeride. Thus it is not certain whether (III) and (IV) are natural plant constituents. Different phæophytins are obtained from (I) and (III), suggesting a difference in the org. portion of the mol. With KOH-EtOH, (I) and (III) afford spectroscopically similar phæopurpurins; (III) probably does not correspond with the hypothetical chlorophyll a<sub>2</sub> of Conant *et al.* (A., 1933, 403).

A. T. P.

**isoOxazole group. X. Nitro-, amino-, and diazo-derivatives of isooxazole.** A. Quilico and C. Musante (*Gazzetta*, 1941, **71**, 327—342).—5-Methylisooxazole with HNO<sub>3</sub> (d 1.51) in H<sub>2</sub>SO<sub>4</sub>-SO<sub>3</sub> at 60—80° gives 4-nitro-, b.p. 187—189°, reduced by SnCl<sub>2</sub>-HCl to the hydrochloride, m.p. 149° (decomp.; darkens from 130°), of 4-amino-5-methylisooxazole (I), b.p. 130°/25—27 mm. (Ac, m.p. 87°, Bz, m.p. 140°, CHPh<sub>3</sub>, m.p. 96—97°, CHPh<sub>3</sub>:CH:CH<sub>3</sub>, m.p. 101°, and m-NO<sub>2</sub>:C<sub>6</sub>H<sub>4</sub>:CH<sub>3</sub>, m.p. 136—137°, derivatives). 3-Methylisooxazole similarly gives 4-nitro-, b.p. 103—107°/25—27 mm., and 4-amino-3-methylisooxazole (II), m.p. 43°, b.p. 118—120°/25 mm. [hydrochloride, m.p. 184° (decomp.); Ac, m.p. 90—91°, Bz, m.p. 148—149°, and CHPh<sub>3</sub>, m.p. 114°, derivatives]. The diazo-compounds from (I) and (II) are labile, but the diazonium chloride from 4-amino-3:5-dimethylisooxazole (obtained as above; cf. Morgan *et al.*, *J.C.S.*, 1921, **119**, 700) with boiling aq. CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> gives CO<sub>2</sub>, Ac<sub>2</sub> (which is also obtained by similar treatment of COAc<sub>2</sub>, the presumed intermediate product), and 5-acetyl-4-methyl-2:1:3-triazole, m.p. 173—174° (Ag salt; oxime, m.p. 202°; p-nitrophenylhydrazine, m.p. 253—255°) (which with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub> is oxidised to 4-methyl-2:1:3-triazole-5-carboxylic acid), and with boiling dil. H<sub>2</sub>SO<sub>4</sub> gives 4-chloro-3:5-dimethylisooxazole, b.p. 151—152° (cf. A., 1939, II, 90) [p-nitrophenylhydrazine, m.p. 235° (decomp.)], and CHClAc<sub>2</sub>, with a substance, C<sub>10</sub>H<sub>14</sub>O<sub>3</sub>N<sub>4</sub> (?) [oxime, m.p. 196—197° (Bz derivative, m.p. 207°); p-nitrophenylhydrazine, m.p. <315° (darkens from 300°)].

E. W. W.

**Substituted sulphonamides.** J. P. English, D. Chappell, P. H. Bell, and R. O. Roblin, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2516).—p-NO<sub>2</sub>:C<sub>6</sub>H<sub>4</sub>:SO<sub>2</sub>:NH<sub>2</sub> and CH<sub>2</sub>Cl-COCl in 4.4% NaOH at 5° give N<sup>1</sup>-chloroacetyl-p-nitro-, m.p. 172—173°, reduced by SnCl<sub>2</sub>-conc. HCl at 35° to N<sup>1</sup>-chloroacetyl-p-amino-benzenesulphonamide, m.p. 157—158°. 2-Benzenesulphonamido-pyridine, m.p. 171—172°, -pyrimidine, m.p. 229—230°, -4-methylpyrimidine, m.p. 193—194°, -thiazole, m.p. 171—172°, and -1:3:4-thiadiazole, m.p. 188—189°, are prepared in C<sub>5</sub>H<sub>5</sub>N. M.p. are corr.

R. S. C.

## VII.—ALKALOIDS.

**Erythrina alkaloids. XIII. Constitution of erythraline, erythramine, and erythratine.** K. Folkers, F. Koniuszy, and J. Shavel, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2146—2151; cf. A., 1943, II, 49).—Indole is obtained from erythraline (I) or erythratine (II) by fusion with KOH. (II) gives an O-benzoate, +2H<sub>2</sub>O, m.p. 248—249°, O-acetate, m.p. 128—129° [hydrolysed by HCl-EtOH-H<sub>2</sub>O to (II)], methiodide, +0.5H<sub>2</sub>O, m.p. 121—125°, [α]<sub>D</sub><sup>25</sup> +109.7° in H<sub>2</sub>O, and anhyd., m.p. 135—136°, [α]<sub>D</sub><sup>25</sup> +110.4° in H<sub>2</sub>O, and thence the N-methyl-methine, C<sub>10</sub>H<sub>23</sub>O<sub>4</sub>N, solid, which with Zn dust gives a gum. H<sub>2</sub>-PtO<sub>2</sub> in H<sub>2</sub>O + a little HBr reduces (II) to dihydroerythraline hydrobromide (III), m.p. 249°, unstable at 25°. Absorption spectra are recorded for erythramine (IV), (I), (II), (III), dihydroerythramine hydrobromide, 6:7-methylenedioxy-1:2:3:4-tetrahydroisoquinoline hydrobromide, and hydrocotarnine. (I), (II), and (IV) contain one CH<sub>2</sub>O<sub>2</sub>, OMe, tert. N common to two nuclei, and 2, 1, and 1 C:C, respectively; (II) contains also a non-phenolic OH; four fused nuclei, of which three are aromatic and common to the three alkaloids and one is variously hydrogenated and oxygenated, are probably present.

R. S. C.

(A.)

The skeleton (A) or, less probably, its linear analogue, is suggested.

## VIII.—ORGANO-METALLIC COMPOUNDS.

**Bivalent and tervalent rhodium. III. Compounds of rhodic halides with tertiary arsines.** F. P. Dwyer and R. S. Nyholm (*J. Proc. Roy. Soc. New South Wales*, 1941, **75**, 140—143).—RhX<sub>3</sub> with AsR<sub>3</sub> in HCl-EtOH gives a sol. form (I) and an insol. form (II), converted by boiling C<sub>6</sub>H<sub>6</sub> into (I). It is suggested that (I) is [RhX<sub>3</sub>.3AsR<sub>3</sub>] whilst (II) is (Rh(AsR<sub>3</sub>)<sub>3</sub>, RhX<sub>3</sub>)'. The following were prepared: diphenylmethylarsinerhodic chloride, m.p. 122—124°

and 176—178°, *bromide*, m.p. 116° and 191°, and *iodide*, m.p. not recorded and 200°; *p-tolyldimethylarsinerhodic chloride*, m.p. (form I) 86—88°, *bromide*, m.p. (form I) 109°, and *iodide*, m.p. 85—86° and 200°.

F. R. G.

## IX.—PROTEINS.

**Present status of mol. wts. of proteins.** A. Rothen (*Ann. New York Acad. Sci.*, 1942, **43**, 229—241).—A general survey.

N. M. B.

**Amino-acid analysis and the structure of proteins.** A. C. Chibnall (*Proc. Roy. Soc.*, 1942, **B**, **131**, 136—160).—A lecture. The recent speculations of Bergmann and Niemann on protein structure are reviewed in the light of new analytical data for certain proteins. The mol. of edestin appears to be a system of 6 similar peptide chains of mol. wt. 50,000, the constituent residues of which conform to the Bergmann-Niemann rule. Lactoglobulin is a system of 8—9 peptide chains, not all of like composition, ovalbumin a similar system of 4 chains. The two latter proteins contradict the rule but the component peptide chains may conform to it. Insulin appears to be a system of 18 peptide chains in agreement with Bernal's deductions from crystallographic data. The conclusion that these protein mols. are systems of peptide chains is based in part on titration data and in part on determinations of free  $\text{NH}_2\text{-N}$ ; the method of linkage of these chains is discussed.

J. H. B.

**Structure of silk fibroin.** E. Abderhalden (*Z. physiol. Chem.*, 1940, **265**, 23—30).—In addition to polypeptide chains, silk fibroin contains large amounts of 2 : 5-diketopiperazines (I) or ring structures closely related thereto. A secondary formation of the isolated (I) from poly- or di-peptides is excluded. Glycylalanine, glycyltyrosine, and alanylserine anhydride have been isolated.

H. W.

**Heats of organic reactions. Digestion of  $\beta$ -lactoglobulin by pepsin.**—See A., 1943, I, 63.

**Oxidative conversion of casein into protein free of methionine and tryptophan.** G. Toennies (*J. Biol. Chem.*, 1942, **145**, 667—670).—Oxidation of casein in  $\text{HCO}_2\text{H}$  solution with  $\text{H}_2\text{O}_2$  converts methionine and probably tryptophan into biologically inactive products and cystine is partly destroyed. Threonine, serine, and probably other  $\text{NH}_2$ -acids are unaffected.

R. L. E.

**Carbon suboxide and proteins. VII. Malonylpepsin.** A. H. Tracy and W. F. Ross (*J. Biol. Chem.*, 1943, **146**, 63—68; cf. A., 1942, II, 241).—Malonylation of the free  $\text{NH}_2$  and phenolic OH of pepsin inactivates the enzyme. Gentle hydrolysis of the O-malonyl linking causes partial reactivation, indicating intimate association between phenolic OH and activity. The specificity of pepsin is unaltered by the presence of  $\text{CO}_2\text{H}$  groups in positions normally occupied by the basic lysyl residues in pepsin; these residues are thus unessential for activity and are without influence on the specificity of the enzyme. Malonylation of serum-albumin increases the no. of peptide linkings subject to the action of pepsin.

A. T. P.

**Brain kephalin, a mixture of phosphatides; separation from it of phosphatidyl-serine and -ethanolamine, and a fraction containing an inositol phosphatide.** J. Folch (*J. Biol. Chem.*, 1943, **146**, 35—44; cf. A., 1941, III, 743).—Brain kephalin (modified method of isolation from fresh ox brain) in  $\text{CHCl}_3$  is fractionated by adding to EtOH; fractions are freed from  $\text{H}_2\text{O}$ -sol. impurities by dialysis. Thus obtained are (a) *phosphatidylethanolamine* (I), sol. in EtOH, which has the composition originally attributed to the whole kephalin, and is hydrolysed to glycerophosphoric acid (II) and  $\text{NH}_2\text{[CH}_2\text{]}_2\text{OH}$ , (b) *phosphatidylserine* (III), and (c) a mixture of phosphatides, one or more of which contains inositol, and which also probably contains some (III); hydrolysis yields inositol, serine, and (II). With the exception of (I), the phosphatides in the kephalin fraction of brain lipins are strongly acidic and are isolated from brain as K or Na salts when treatment with mineral acid is avoided in isolation.

A. T. P.

## X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

**Colour test for citrinin. Its preparation.** H. Tauber, S. Laufer, and M. Goll (*J. Amer. Chem. Soc.*, 1942, **64**, 2228—2229).—Prep. of citrinin from *P. citrinum* is outlined. With  $\text{H}_2\text{O}_2$ -EtOH- $\text{H}_2\text{O}$  it becomes yellow, changed to red by NaOH. The yellow-red change is reversible by  $\text{H}_2\text{SO}_4$ -NaOH. Cultures give the same reaction; penicillin does not. Exposure in dioxan causes a similar, but in EtOH a different, change.

R. S. C.

**Notatin: an anti-bacterial glucose-aerodehydrogenase from *Penicillium notatum*, Westling.**—See A., 1943, III, 143.

## XI.—ANALYSIS.

**Use of concentrated sulphuric acid instead of lead dioxide for the absorption of oxides of nitrogen in micro-C-H determinations.** K. Burger (*Angew. Chem.*, 1942, **55**, 260—261).— $\text{H}_2\text{O}$  is absorbed in  $\text{Mg}(\text{ClO}_4)_2$ , then N oxides in  $\text{H}_2\text{SO}_4$ , and then  $\text{CO}_2$  as usually. The  $\text{H}_2\text{SO}_4$  may be reactivated by passing  $\text{O}_2$  through it at 150°.

J. W. S.

**Quantitative decomposition of organic bromine and iodine compounds by the lime fusion method.** W. M. MacNevin and G. H. Brown (*Ind. Eng. Chem. [Anal.]*, 1942, **14**, 908).—The method previously described for determination of Cl (A., 1940, II, 263) can be applied to org. Br and I compounds.

J. D. R.

**Steam-distillation apparatus for micro-Kjeldahl analysis.**—See A., 1943, III, 76.

**Reduction of unsaturated hydrocarbons at the dropping mercury electrode.**—See A., 1943, I, 64.

**Determination of inulin.**—See A., 1943, III, 152.

**Dissociation constants of diphenylselenium dibromide and diiodide.**—See A., 1943, I, 61.

**Potentiometric studies in oxidation-reduction reactions. XI. Quantitative potentiometric determination of aromatic amines.** B. Singh and A. Rehmann (*J. Indian Chem. Soc.*, 1942, **19**, 349—353).—By the use of a bright Pt electrode in the titration liquid, in conjunction with a calomel electrode, *o*- and *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2$ , 1 : 2 : 4- $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NH}_2)_2$ , *o*- and *p*- $\text{NH}_2\text{C}_6\text{H}_4\text{OH}$ , *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ , and  $\text{NHPh}_2$  can be accurately determined potentiometrically. The first three are titrated in aq. HCl against standard  $\text{KIO}_3$ , and the others are titrated in (usually) aq.  $\text{H}_2\text{SO}_4$  with standard  $\text{NaNO}_2$ .

F. L. U.

**Microbiological method for determination of *p*-aminobenzoic acid.** M. Landy and D. M. Dicken (*J. Biol. Chem.*, 1943, **146**, 109—114).—The method is based on the growth response of *Acetobacter suboxydans* to *p*- $\text{NH}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$  (I); turbidity is measured with a photo-electric colorimeter. No growth occurs in the basal medium in absence of (I). Materials insol. in  $\text{H}_2\text{O}$  are first finely-divided, extracted with 10—20 vols. of  $\text{H}_2\text{O}$  for 30 min. at 15 lb., centrifuged, and filtered. The inhibitory action of blood, c.s.f., etc. on the test organism is overcome by autoclaving. (I) is widely distributed, e.g., in brewer's yeast, liver extract, fresh liver, and meat extract, and probably in most body tissues. The activity of other compounds similar to (I), viz., *p*-amino-phenylacetic acid, -ethyl benzoate, -phenylglycine, etc., is not comparable with that of (I), and thus the method has high specificity.

A. T. P.

**Determination of the tocopherols and tocopherylquinones by the colorimetric oxidation-reduction method.** J. V. Scudi and R. P. Buhs (*J. Biol. Chem.*, 1943, **146**, 1—6; cf. A., 1941, III, 685; 1942, III, 702).—The sample containing tocopherols (I) is dissolved in BuOH,  $\text{AuCl}_3$  added, and the mixture kept in the dark at room temp. for 30 min.; aq. technical hexane is added; the org. layer is washed and conc. in vac. under  $\text{N}_2$ . Reduction is effected using Raney Ni in BuOH with phenosafranine (II) as indicator, and the solution is pumped into standard 2 : 6-dichlorophenol-indophenol (III). Vitamin-K quinol reduces (III) immediately, but tocopherylquinones (IV) act more slowly (40—60 min.) and are estimated by difference. The specificity of the method can be increased by preliminary reductive treatment with Claisen's alkali. Substances to be tested must be oil-sol. and non-reducing, and with  $\text{AuCl}_3$  give new substances capable of reversible reduction and oxidation, which have an oxidation-reduction potential  $>$  that of (II) but  $<$  that of (III), and which must reduce (III) slowly. Carotenoids and vitamin-A do not interfere. (I) and (IV) in the same sample are best determined by two analyses, although this is not essential, as (I) can be recovered by light petroleum after determining (IV), and then oxidised further. Results are given for wheat-germ oil, refined cottonseed oil, dog plasma, and whole human blood [(IV) not observed previously]. The difference in biological activity between  $\alpha$ - and  $\beta$ - +  $\gamma$ -tocopherols is discussed, and a method of differentiating suggested, viz.,  $\beta$ - and  $\gamma$ - with  $\text{HNO}_2$  give (probably) *o*-quinones, whereas  $\alpha$ - apparently does not react.

A. T. P.

**Determination of lanthionine.** W. C. Hess and M. X. Sullivan (*J. Biol. Chem.*, 1943, **146**, 15—18).—Lanthionine (I) is converted into cysteine (II) by colourless 57% HI containing 1% of  $\text{KH}_2\text{PO}_2$  at 135—140° (in  $\text{N}_2$ ). Neither cystine nor methionine interferes with the determination of (I). (I) formed by dil. alkali treatment of a protein such as wool or lactalbumin can be determined colorimetrically by first hydrolysing the (I)-containing protein with HCl; (I) does not react in the Sullivan cystine or cysteine reactions. Then total (II) is measured after hydrolysis of the protein with HI. The difference between the two hydrolysates gives amount of (II) derived from (I), which multiplied by 1.72 gives amount of (I).

A. T. P.

## A., II.—Organic Chemistry

APRIL, 1943.

## I.—ALIPHATIC.

Semiquantitative extension of the electronic theory of the English school. A. E. Remick (*J. Org. Chem.*, 1942, 7, 534—545).—The author advocates the summation of  $\Delta H$  for all linkings made and broken in the rate-controlling step as the best method for judging the most probable reaction path. If this summation is made correctly taking into account the interaction between all the linkings involved the val. of  $\Delta H$  finally obtained should be the heat of activation. Such calculations can be made with fair accuracy for simple compounds on the basis of the theory of abs. reaction rates. If these interactions are neglected and a simple summation is made of the  $\Delta H$  vals. for the linkings made and broken, the results give a reasonably safe guide for comparing reactions involving unsubstituted, unconjugated compounds and hence form a semiquant. extension of the electronic theory of the English school. Since the method aims only at establishing a sequence of the relative probabilities of different conceivable rate-controlling steps, the calculations can be further simplified by omitting from consideration all of the  $\Delta H$  terms for linkings which would occur in both or all of the reactions under consideration and which would accordingly cancel out in the final comparison. The resultant vals. of  $\Delta H$  are designated "comparative heats of activation." Considerations are applied to (a) addition of halogens to  $C_2H_4$  in which it is established that the most probable mechanism is  $CH_2:CH_2 + Cl_2 \rightleftharpoons$

$\dot{C}H_2:\dot{C}H_2--\dot{C}l-\dot{C}l \rightarrow CH_2Cl-\dot{C}H_2 + \dot{C}l$ , that the reaction will lead to addition rather than to substitution, that  $C_2H_4$  is the nucleophilic reagent in this reaction which may accordingly be placed in class A of the Ingold-Rothstein scheme, and that the velocity of halogen addition is  $Cl_2 > Br_2 > I_2$ ; (b) addition of H halides to olefins in which the rate-controlling step is  $CR_2:CH_2 + HX \rightarrow CR_2:CH_2-H-X$  and the predicted order of velocity (neglecting entropy factors) is  $HI > HBr > HCl$ ; (c) hydrolysis of chlorides of N and P in which the relative probabilities of the mechanisms are  $XCl_3 + H^+ \rightleftharpoons XCl_2--Cl-H \rightarrow ClX^+ + HCl > XCl_3 + H^+ \rightleftharpoons H--XCl_2--Cl \rightarrow HXCl_2 + Cl^- > XCl_3 + OH^- \rightleftharpoons Cl_2X--Cl--OH \rightarrow Cl_2X + HOCl$ . On the assumption that the 3 Cl atoms are removed by the same mechanism  $PCl_3$  should yield  $HCl$  and  $P(OH)_3$ . For  $NCl_3$  the comparative heats of activation for the three mechanisms are  $-58.6$ ,  $-43.4$ , and  $+76.8$  kg.-cal. Hence the second mechanism is the more probable and  $NCl_3$  would be expected to yield  $HOCl$  and  $NH_3$  on hydrolysis; (d) hydrolysis of alkyl halides which in acid solution is shown to follow the mechanism  $MeX + AqH^+ \rightleftharpoons Me-X-H^+ + Aq \rightarrow Me^+ + HX + aq$ ; (e) cyanohydrin formation with aldehydes for which a more facile addition is predicted in a basic than in an acidic medium; (f) reactions of ethers with halogen hydrides etc. which probably follow the course,  $MeOMe + HX \rightleftharpoons MeO(Me) \cdot H-X \rightarrow MeOH + X' + Me^+$ , and (g) reactions of alcohols with halogen hydrides in which the order of reactivity is calc. to be *tert.* > *sec.* > *primary*. H. W.

"Sliding" isomerism ("olisthomerism"). A. Balandin (*Acta Physicochim. U.R.S.S.*, 1942, 16, 195—205).—Where it is possible by change of groups in different ways to arrive at the same compound from the same starting materials, the products are called "sliding" isomerides or olisthomerides. Thus, in the formation of  $MeOAc$  from  $AcOH$  and  $MeOH$ , the substances may combine as follows:  $Me:OH + MeCO:OH$  and  $Me:OH + MeCO \cdot O:H$ . Conditions for the existence of this type of reaction are outlined. Reactions in which it may take place include esterification, formation of ethers from alcohols, formation of mixed acid anhydrides, mixed ketones, aldehydes from formic and another carboxylic acid, *sec.* amines from two primary amines, and the reaction between two different peroxides, etc. The investigation of the reactions provides an important method for comparing the strengths of linkings and the mobility of groups and atoms. Isotopes, artificial radioactivity, and optical activity can also be introduced into the study of the phenomenon. A. J. M.

Stereochemistry. III. Preparation of *d*- $\alpha$ -deutero- $\beta$ -methylbutane. Its optical rotation. H. C. Brown and C. Groot (*J. Amer. Chem. Soc.*, 1942, 64, 2563—2566).—*d*- $CHMeEt \cdot CH_2 \cdot OH$  (from fusel oil) and  $SOCl_2-C_5H_5N$  give *d*- $CHMeEt \cdot CH_2Cl$ , b.p.  $99.5^\circ/750$  mm.,  $\alpha_D^{25} +1.33^\circ$ , the Mg derivative of which with  $HCl$  gives  $EtPr^\beta$  and

with  $DCl$  gives *d*- $CHMeEt \cdot CH_2D$ , b.p.  $27^\circ/746$  mm.,  $\alpha_{5461} < 0.005^\circ$ , probably  $< 0.002^\circ$ . R. S. C.

Isomerisation of *n*-pentane.—See B., 1943, II, 2.

Industrial synthesis of hexachloroethane. II. Chlorination of tetrachloroethane.—See B., 1942, II, 417.

Cyclic production of nitroparaffins.—See B., 1943, II, 38.

Synthesis of ethylenic and saturated hydrocarbons of *iso*-structure with a quaternary carbon atom. II. Reaction between  $\beta$ -bromo- $\beta\delta$ -dimethyl- $\Delta^2$ -pentene and magnesium alkyl halides. R. J. Levina and J. B. Kagan (*J. Gen. Chem. Russ.*, 1941, 11, 523—526).— $CMe_2:CH \cdot CMe_2Br$  and  $MgRX$  ( $X = Cl, Br$ ) yield the hydrocarbons  $CMe_2:CH \cdot CMe_2R$  ( $R = Me, Et$ , b.p.  $132^\circ$ , *Pr*<sup>a</sup>, b.p.  $152-153.5^\circ$ ). These are hydrogenated to the hydrocarbons  $CMe_2Bu^\beta R$  ( $R = Me, Et$ , b.p.  $129-130^\circ$ , *Pr*<sup>a</sup>, b.p.  $151-152^\circ$ ). R. T.

Stability of butadiene in nitrogen mixtures at  $250-500^\circ$ .—See B., 1943, II, 1.

Photo-addition of hydrogen bromide to olefinic linkings. W. E. Vaughan, F. F. Rust and T. W. Evans (*J. Org. Chem.*, 1942, 7, 477—489).—"Abnormal" addition of  $HBr$  to olefinic linkings ( $CH_2:CHMe$ ,  $CH_2:CHEt$ ,  $CH_2:CH \cdot CH_2Br$ , diallyl) has been effected photometrically in liquid and vapour phase without the intervention of  $O_2$  or peroxides. In the liquid phase, quant. conversions can be obtained so rapidly that the method suggests itself for practical syntheses; irradiation with sufficiently short  $\lambda$  is the principal requirement. Some photo-dissociable materials (aldehydes, ketones, metal alkyls) are able to sensitise the "abnormal" addition even when the radiation used is not absorbed by  $HBr$  or the olefine. Certain materials ( $Mel, I$ ) are powerful inhibitors of the gas-phase process. All the evidence substantiates previous conclusions that the mechanism of the "abnormal" addition is a chain reaction involving Br atoms and free radicals. H. W.

Olefine-oxygen-hydrogen bromide photo-reaction. F. F. Rust and W. E. Vaughan (*J. Org. Chem.*, 1942, 7, 491—496).—The presence of large concns. of  $O_2$  inhibits the photo-reaction of olefines ( $C_2H_4$  and  $C_3H_6$ ). The products of these retarded reactions include the *n*-monobromide, dibromide, bromohydrin, and  $H_2O$ . In the case of  $C_3H_6$ ,  $CH_2AcBr$  is also formed. Peroxidic compounds are not found.  $CH_2AcBr$  (and, by analogy, any  $\alpha$ -Br-ketone) acts as a powerful catalyst for the "abnormal" addition of  $HBr$  to olefines, even in the dark. H. W.

Cetene ( $\Delta^2$ -hexadecene). H. Suida and F. Drahowzal (*Ber.*, 1942, 75, [B], 991—997).—Evidence is adduced in favour of the view that homogeneous  $\Delta^2$ -hydrocarbons are obtained from Mg alkyl chlorides and allyl halides.  $n-C_{12}H_{25}Cl$  is converted by  $KCN$  into *n*-trideconitrile, b.p.  $150.6^\circ/10.5$  mm., reduced by the rapid action of a slight excess of Na in boiling  $Bu^aOH$  to *n*- $C_{13}H_{27} \cdot NH_2$ , the hydrochloride of which is transformed by  $BzCl$  in  $C_6H_6$  at  $108-110^\circ$  into *benz*-tridecylamide, m.p.  $70.6^\circ$ . This is converted by  $PCl_5$  into *n*- $C_{13}H_{27}Cl$ , b.p.  $135.7-136^\circ/9$  mm. (corresponding bromide, b.p.  $148-149^\circ/9.5$  mm., m.p.  $6.0^\circ$ ), transformed by the successive action of Mg and  $CH_2:CH \cdot CH_2Br$  into  $\Delta^2$ -hexadecene (cetene). H. W.

Addition of iodine trichloride to acetylene and the structure of  $\beta$ -chlorovinyl iodochloride. R. C. Freidlina and A. N. Nesmejanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 892—894).—Addition of  $ICl_3$  to  $C_2H_2$  in either 3% or 15%  $HCl$  gives  $\beta$ -chlorovinyl iodochloride (I), m.p.  $74^\circ$ , identical with the substance obtained by addition of  $Cl_2$  to  $CHCl:CHI$ .  $C_2H_2$  is eliminated from (I) by treatment with  $CsCl$  or  $C_5H_5N$ . A solution of (I) in  $CHCl_3$  with  $C_5H_5N$  gives a ppt. of a double compound of (I) and  $C_5H_5N$ , reduced by  $FeSO_4$  with evolution of  $I$ . F. R. S.

Purification of methanol.—See B., 1943, II, 39.

Constitution of pyrlyene: chemical evidence. H. Sargent, E. R. Buchman, and J. P. Farquhar (*J. Amer. Chem. Soc.*, 1942, 64, 2692—2693; cf. A., 1943, I, 54).—Degradation of 1:1-dimethyl-2-bromo-methylpyrrolidinium bromide gives mixed bases (A) (70%), b.p.  $\sim 56-70^\circ/50$  mm. (cf. lit.), from which 13% of a stable base,  $C_7H_{13}N$ , b.p.  $65^\circ/49$  mm. (diluturate, m.p.  $161-162^\circ$ ; picrate, m.p.  $100.5-101^\circ$ ), is obtained. The derived methiodide (I), m.p.  $259^\circ$  (decomp.) (lit.  $257^\circ$ ) (corresponding methopicate, m.p.  $112.5-113^\circ$ ), is also

obtained from (A); it is stable to  $H_2O$  at  $100^\circ$  and resists hydrogenation, but gives the methochloride which with  $H_2$ -Pd-C in  $H_2O$  at 2 atm. yields  $n-C_5H_{11} \cdot NMe_3X$ . Distilling (I) with conc. aq. KOH gives pyrlyene (II) (59—73%), b.p.  $59.4^\circ/744$  mm., which is shown to be  $CMe_2C \cdot CH_2$  by physical properties, addition of 3  $H_2$  (Pd-C) to give  $n-C_5H_{12}$  and of HCl to give  $CHMe \cdot CCl \cdot CH_2CH_2$  [1:4- $O:C_{10}H_8:O$  adduct, m.p.  $180.7$ — $181^\circ$ ; (II) does not react at  $100^\circ$ . M.p. are corr. R. S. C.

**Octadecyl alcohol (3:5-dinitrobenzoate, m.p.  $77.5^\circ$ ) etc. in gorgonias.**—See A., 1943, III, 181.

**Silico-organic compounds. IV. Action of organic acid halides and of hydrohalogen acids on silico-orthoesters.** H. W. Post and H. M. Norton (*J. Org. Chem.*, 1942, 7, 528—533).— $Si(OEt)_4$  and  $AcCl$  (1:1) at  $135^\circ$  give  $SiCl(OEt)_3$  in 90% yield. At  $185^\circ$  and with ratio 1:2 there is a fair yield of impure  $SiCl_2(OEt)_2$  whilst with ratio 1:5 some  $SiCl_3(OEt)$  is produced. At  $200^\circ$  in a steel bomb with ratios 1:2 and 1:1 only  $EtOAc$  could be identified, spongy siliceous polymerides being also produced. At  $185^\circ$   $Si(OBu^a)_4$  and  $AcCl$  (1:1) give  $SiCl(OBu^a)_3$ . A boiling equimol. mixture of  $Si(OEt)_4$  and  $BzCl$  gives 70% of  $SiCl(OEt)_3$  and 88% of  $EtOBz$ . With ratio 1:4 an identifiable product does not result.  $Si(OEt)_3 \cdot OAc$  and  $AcCl$  (1:2) do not react at  $40^\circ$ . At  $185^\circ$  and with ratio 1:1 there is no well-defined product; this is also the case with  $Si(OEt) \cdot O \cdot COEt$ .  $AcBr$  and  $Si(OEt)_4$  (1:1) at  $18.5^\circ$  give 20% of  $EtBr$ , 80% of  $EtOAc$ , but no homogeneous compound of Si. Similarly  $BzBr$  gives 26% of  $EtBr$  and 68% of  $EtOBz$ .  $AcBr$  and  $Si(OBu^a)_4$  give  $Bu^aBr$ , probably  $Bu^aOAc$ , and a little  $SiBr(OBu^a)_3$ . The possibility that  $Bu^a_2O$  is an intermediate is excluded experimentally. Passage of dry HCl through  $Si(OEt)_4$  at room temp. gives a small amount of  $EtOH$ , mainly unchanged ester, and some polymerised compounds of Si. At  $185^\circ$   $Si(OEt)_4$  and HCl appear to afford  $EtCl$ . Reaction does not appear to occur between  $Si(OBu^a)_4$  and HCl.  $HBr$  and  $Si(OEt)_4$  appear to react more readily, giving  $EtBr$  and  $EtOH$ , whilst  $Si(OBu^a)_4$  gives some  $Bu^aBr$  and very little  $Bu^aOH$ .  $Si(OEt)_4$  and  $Si(OBu^a)_4$  and HI yield the corresponding alcohol and iodide. H. W.

**Mechanism of obtaining vinyl ethers.** E. S. Vasserman and A. B. Bedrintzeva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 34—36).—The kinetics of the reaction of vinylation of alcohols are studied. When  $C_2H_2$  reacts with 96.5%  $EtOH$  in presence of KOH at  $170$ — $190^\circ/\sim 30$  atm., the first stage is probably activation of  $C_2H_2$ , which then reacts with  $EtOH$  to give  $CH_2:CH \cdot OEt$ . It is assumed that  $EtOH$  reacts only with dissolved  $C_2H_2$ , the concn. of which is approx. const. owing to large excess of it in the gaseous phase and the relatively high temp. A. T. P.

**aaa-Trichloro- $\gamma$ -nitro- $\beta$ -hydroxyalkanes and their reduction products.** S. Malkiel and J. P. Mason (*J. Amer. Chem. Soc.*, 1942, 64, 2515).— $CCl_3 \cdot CH(OH) \cdot CHR \cdot NO_2$  (from  $CCl_3 \cdot CHO$ ,  $H_2O$ ,  $CH_2R \cdot NO_2$ , and aq.  $K_2CO_3$  at  $50$ — $52^\circ$ ) with  $H_2$ -Raney Ni in  $EtOH$  at room temp./55 lb. give aaa-trichloro- $\gamma$ -amino- $\beta$ -hydroxy-propane (I), m.p.  $44.7$ — $45.7^\circ$  (corr.) (lit.  $42$ — $43^\circ$ ), b.p.  $138$ — $146^\circ/13$  mm. ( $Bz$  derivative, m.p.  $167.4^\circ$ ), -n-butane, b.p.  $138$ — $140^\circ/9$  mm. ( $Bz$  derivative, m.p.  $182.5^\circ$ ), and -n-pentane, b.p.  $136$ — $142^\circ/10$  mm. ( $Bz$  derivative, m.p.  $195.2^\circ$ ). Addition of  $COMe_2$  to (I) in  $EtOH$  gives a compound,  $C_3H_6ONCl_3$ , m.p.  $167.4$ — $167.7^\circ$  (corr.). R. S. C.

**Purification of pentaerythritol.**—See B., 1942, II, 419.

**Preparation of divinyl ether.**—See B., 1943, II, 3.

**Ethyl peroxides. XIV. Oxidation of diisopropyl ether.** A. Rieche and K. Koch (*Ber.*, 1942, 75, [B], 1016—1028).—A sample of  $Pr^i_2O$  which had been kept in a metal container for 10 years contained trimeric (I), m.p.  $98.5^\circ$ , and dimeric (II), m.p.  $131^\circ$ , acetone peroxide,  $COMe_2 \cdot H_2O_2$ , and some  $Pr^iOH$ ,  $AcOH$ , and  $HCO_2H$ . Oxidation appears to proceed thus:  $Pr^i_2O + O_2 \rightarrow Pr^iO \cdot CMe_2 \cdot O_2H$  (III); (III) +  $H_2O \rightarrow OH \cdot CMe_2 \cdot O_2H$  (IV) +  $Pr^iOH$  and (III)  $\rightarrow CMe_2 \cdot O_2 \cdot$  (becomes polymerised) +  $Pr^iOH$ ; (IV)  $\rightarrow COMe_2 + H_2O$ .  $Pr^i_2O + 2O_2 \rightarrow O(CMe_2 \cdot O_2H)_2$  (V); (V) +  $H_2O \rightarrow 2(IV)$  (forms acetone peroxide); (V)  $\rightarrow H_2O + 2CMe_2 \cdot O_2 \cdot$  (becomes polymerised); (IV)  $\rightarrow COMe_2 + H_2O_2$ . In boiling  $C_6H_6$  or  $EtOH$  the mol. wt. of (I) agrees with the expected val. whereas that of (II) in boiling  $C_6H_6$ ,  $EtOH$ ,  $EtOAc$ , and  $COMe_2$  is very variable. (II) is much more volatile, more sensitive to shock, and more explosive than (I). (II) is hydrolysed by acid considerably more rapidly than (I). The absorption spectra of (I) and (II) are recorded. H. W.

**Keten acetals. XI. Pyrolysis of keten acetals and ortho-esters.** S. M. McElvain, H. I. Anthes, and S. H. Shapiro (*J. Amer. Chem. Soc.*, 1942, 64, 2525—2531; cf. A., 1943, II, 23).—The reaction,  $CHX:C(OEt)_2$  ( $X = H, Cl, alkyl$  etc.)  $\rightarrow CH_2X \cdot CO_2Et + C_2H_4$ , occurs in glass at  $200^\circ$  (6 hr.; yield 20—100% dependent on the drying and usage of tubes), in cyclohexane in steel at  $200^\circ$  (5—10% yield), or by rapid passage over glass chips,  $MnO_2$ ,  $Al_2O_3$ ,  $ZnO$ , or  $CrO_3$  at  $300$ — $400^\circ$  (60—80% yield). However, keten  $Me_2$  acetal (I), b.p.  $89$ — $91^\circ/740$  mm., is 95% unchanged after heating for 24 hr. at  $200^\circ$ .  $CMe(OMe)_3$  and  $Br$  give  $Me_3$  orthobromoacetate (70%), b.p.  $74$ — $75^\circ/17$  mm., which with  $Na$  gives 70% of (I).  $CH_2:CH \cdot OAc$  with  $Br$  and then  $CH_2:CH \cdot CH_2 \cdot OH$  (II) or  $CH_2Ph \cdot OH$  at  $5^\circ$  and

later room temp. gives diallyl (45%), b.p.  $101$ — $102^\circ/20$  mm., and  $(CH_2Ph)_2$  bromoacetal (75%), b.p.  $190$ — $195^\circ/2$  mm., respectively, which with  $KOBu^t \cdot Bu^tOH$  at the b.p. give, doubtless by way of the keten acetal, allyl  $\Delta^2$ -pentenoate (43%), b.p.  $48$ — $50^\circ/8$  mm.,  $160$ — $162^\circ/740$  mm. [hydrolysed to (II) and  $CH_2:CH \cdot [CH_2]_2 \cdot CO_2H$ ], and  $CH_2Ph$  o-tolylacetate (46%), b.p.  $158$ — $162^\circ/1.5$  mm. (hydrolysed to  $CH_2Ph \cdot OH$  and o- $C_6H_4Me \cdot CH_2 \cdot CO_2H$ ), respectively.  $CH_2X \cdot C(OEt)_3$  ( $X = H, Cl, or OEt$ ) decomposes at  $200^\circ$  into  $CH_2X \cdot CO_2Et$ ,  $EtOH$ , and  $C_2H_4$ ; proof that the reaction occurs by way of  $CHX:C(OEt)_2$  is provided by decomp. of  $CMe(OEt)_3$  in presence of  $PhOH$  at  $200^\circ$  to  $EtOAc$ ,  $EtOH$ , and  $PhOEt$ , and of  $OEt \cdot CH_2 \cdot C(OEt)_3$  similarly into  $OEt \cdot CH_2 \cdot CO_2Et$  (47%) +  $OEt \cdot CH_2 \cdot CO_2Ph$  (53%),  $EtOH$ , and  $C_2H_4$ . Similarly,  $CMe(OR)_2 \cdot OR'$  [prep. from  $CH_2:C(OR)_2$  and  $R'OH$ ] gives (a)  $R'OH + CH_2:C(OR)_2 \rightarrow (+PhOH) CMe(OR)_2 \cdot OPh \rightarrow ROAc + PhOR$  and (b)  $ROH + CH_2:C(OR) \cdot OR' \rightarrow (+PhOH) OR \cdot CMe(OR') \cdot OPh \rightarrow (c) R'OAc + PhOR$ , and (d)  $ROAc + PhOR'$ . The relative amounts in which these reactions occur are determined for  $R = Et$ ,  $R' = Bu^a, Bu^b, sec-Bu, isoamyl, CH_2Bu^t$ , and  $CH_2Ph$ , and for  $R = Bu^a$ ,  $R' = Et$ ; they follow expectations.  $CMe(OEt)_2 \cdot O \cdot CH_2Ph$  alone gives 84% of  $CH_2:C(OEt) \cdot O \cdot CH_2Ph$  and thence  $\sim 14\%$  of o- $C_6H_4Me \cdot CO_2Et$ , b.p.  $78$ — $83^\circ/3$  mm. With  $CH_2Br \cdot C(OEt)_3$  and  $CHBr_2 \cdot C(OEt)_3$  decomp. as above is complicated by loss of  $EtOBr$  ( $\rightarrow MeCHO + HBr$ ) and by addition of  $HBr$  to the keten, leading to varied products.  $CPh(OEt)_3$  at the b.p. gives  $EtOBz$  (60%) and  $Et_2O$ . The following are described.  $Et_2Bu^a$ , b.p.  $70$ — $72^\circ/15$  mm.,  $Bu^b$ , b.p.  $64$ — $66^\circ/14$  mm., sec- $Bu$ , b.p.  $63$ — $65^\circ/15$  mm., isoamyl, b.p.  $80$ — $82^\circ/15$  mm., neopentyl, b.p.  $87$ — $88^\circ/28$  mm., and benzyl, b.p.  $121$ — $122^\circ/8$  mm., orthoacetate;  $EtBu^a_2$  orthoacetate, b.p.  $98$ — $100^\circ/13$  mm.;  $Ph$  sec- $Bu$  ether, b.p.  $184$ — $185^\circ$ . R. S. C.

**Addition of sulphuric acid to olefines of high mol. wt.** P. Baumgarten (*Ber.*, 1942, 75, [B], 977—983).—Dodecene obtained by dehydrating dodecan- $\alpha$ -ol with hot, highly conc.  $H_3PO_4$  or by the thermal decomp. of dodecyl palmitate is oxidised by  $BzO_2H$  to the corresponding oxide, which is hydrolysed by very dil.  $H_2SO_4$  to the glycol and then quantitatively oxidised by  $Pb(OAc)_4$ . The substance obtained by the second reaction is thus shown to be  $\Delta^a$ -dodecene (I) whereas the first method affords a mixture (II) of  $\Delta^b$ - and  $\Delta^c$ -dodecene. Most complete action between (I) or (II) and  $H_2SO_4$  is obtained by rapid use of a moderate excess of the monohydrate at  $\sim 0^\circ$ , whereby 86% of alkyl sulphate can be produced. (I) gives a non-uniform product separable by  $CHCl_3$ ,  $COMe_2$ , light petroleum,  $C_6H_6$ , etc. into the sparingly sol. Na  $\beta$ -dodecyl sulphate (III) and freely sol. Na  $\gamma$ -,  $\delta$ -, and possibly  $\epsilon$ -dodecyl sulphates (IV). The  $\alpha$ -dodecyl compound (V) could not be detected. (III) is identified by hydrolysis to dodecan- $\beta$ -ol, oxidised to dodecanone. Hydrolysis of (IV) gives a mixture of sec. alcohols oxidised to a mixture of ketones. Migration of  $SO_4$  occurs during the action of  $H_2SO_4$  on (III) whereby salts sol. in  $CHCl_3$  are produced in considerable proportion whereas (V) is unchanged by this treatment. Similarly (IV) is partly converted into (III) by  $H_2SO_4$ . H. W.

**Nature of the glycerophosphoric acid present in phosphatides.** J. Folch (*J. Biol. Chem.*, 1943, 146, 31—33).—Methods of isolation used to prepare glycerophosphoric acid (I) from phosphatides hydrolysed with acid or alkali yield optically active mixtures of  $\alpha$ - +  $\beta$ -acids, and there is no evidence to show whether (I) in phosphatides is in  $\alpha$ - or  $\beta$ -form. A. T. P.

**Photo-addition of hydrogen sulphide to olefinic linkings.** W. E. Vaughan and F. F. Rust (*J. Org. Chem.*, 1942, 7, 472—476).—Ultra-violet radiation of short  $\lambda$  readily promotes the addition of  $H_2S$  to  $CH:CHEt$ ,  $CH_2:CHMe$ , diallyl,  $CH_2:CHCl$ , diallyl ether, and  $CH_2:CH \cdot CO_2Me$  with formation of mercaptans and sulphides. Light of  $\lambda$  transmissible by Pyrex is effective in initiating reaction if a small amount of photo-dissociable material such as  $COMe_2$  is present. S of the  $\cdot SH$  or  $\cdot S \cdot$  adds exclusively to C of the double linking which has the largest no. of H atoms.  $H_2S$  and olefine combine slowly in the gas phase under the influence of ultra-violet radiation. The mechanism is one of a free radical chain and is dependent on the preliminary dissociation of  $H_2S$ . H. W.

**Solubilities of saturated fatty acids.**—See A., 1943, I, 87.

**Mechanism of oxidation of oleic and elaidic acids and their methyl esters by hydrogen peroxide in acetic acid. Configurations of  $\theta$ -dihydroxystearic acids.** G. King (*J.C.S.*, 1943, 37—38).—With  $H_2O_2$  in  $AcOH$  at room temp., oleic acid yields mixed monoacetates (also obtained from oleic acid epoxide, m.p.  $59.5^\circ$ , and  $AcOH$  at room temp.) of dihydroxystearic acid, m.p.  $95^\circ$ , whilst elaidic acid gives some elaidic acid epoxide (I), m.p.  $55.5^\circ$ , and monoacetates [also obtained (with 50% of unchanged epoxide) from (I) and  $AcOH$ ] of dihydroxystearic acid, m.p.  $132^\circ$ . Me oleate and elaidate behave similarly. Traces of peroxides are produced in all cases. It is concluded that in the oxidation in  $AcOH$  the epoxides are first formed, and by fission and inversion give the  $(OH)_2$ -acids. A. Li.

**Autoxidation of oxygen-active acids. V. Viscosimetric and volumetric analysis of the addition of oxygen to the triglycerides.** W. Treibs (*Ber.*, 1942, 75, [B], 953—957; cf. A., 1942, II, 392).—

Quant. viscosimetric and volumetric analysis of the addition of  $O_2$  to glyceryl oleate dilinoleate from soya-bean oil and glyceryl linoleate dilinoleate from linseed oil shows that the autoxidative behaviour of the glycerides is an additive function of that of the individual active chains. As in the case of the corresponding Me ester, the glycerides form initially monomeric peroxides; these subsequently undergo condensation and dehydration. In the drying of the corresponding vegetable oils, the glyceryl residues are responsible for the film-building capacity and form the points of union of the macromol. film nets. H. W.

**Preparation of tartaric acids.**—See B., 1943, II, 41.

**Preparation of crystalline anhydrous citric acid.**—See B., 1943, II, 41.

**Preparation of sodium pyruvate.** W. v. B. Robertson (*Science*, 1942, 96, 93—94).—Pptn. by approx. equiv. amount of NaOH-EtOH from  $AcCO_2H \cdot EtOH$  gives an 80% yield after recrystallisation. E. R. R.

**Preparation of calcium gluconate.**—See B., 1943, II, 37.

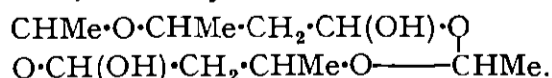
**Condensations. XVII. Acylation of the anions of alkyl esters by phenyl esters. Preparation of ethyl propionylacetate and related  $\beta$ -keto-esters.** B. Abramovitch and C. R. Hauser (*J. Amer. Chem. Soc.*, 1942, 64, 2271—2274; cf. A., 1942, II, 132).—Treating ROAc with  $NaCPh_3$  and then with  $EtCO_2R'$  gives  $EtCO \cdot CH_2 \cdot CO_2R$  and  $R'OH$ ; R and  $R'$  must be chosen so as to allow ready separation of the products. Adding EtOAc and then *p*-diphenyl propionate [prep. from *p*- $C_6H_4Ph \cdot OH$ , NaOH, and  $(EtCO)_2O$  at  $\sim 5^\circ$ ] to  $NaCPh_3$  in  $Et_2O-N_2$  at  $-5^\circ$  and later keeping at  $15^\circ$  gives *El propionylacetate* [ $\beta$ -keto-*n*-valerate] (I) (44%), b.p.  $91-92^\circ/17$  mm.; use of  $EtCOCl$  gives 32% of  $(EtCO)_2CH \cdot CO_2Et$  and thence 16% of (I). *n*- $C_5H_{11} \cdot OAc$  with  $NaCPh_3$  and  $EtCO_2Ph$  gives 30% of *n*-amyl propionylacetate, b.p.  $113-115^\circ/10$  mm.  $Bu^iCO_2Et$  with  $NaCPh_3$  and  $EtCO_2Ph$  gives 58% of  $EtCO \cdot CHPr^i \cdot CO_2Et$ , b.p.  $107-109^\circ/21$  mm. *Bu*<sup>*y*</sup> cyanoacetate [prep. from  $CH_2Br \cdot CO_2Bu^y$  and  $KCN \cdot MeOH$ ], b.p.  $107-108^\circ/23$  mm., with  $MgEtBr \cdot Et_2O$  gives a complex mixture.  $COMeEt$  with  $NaCPh_3$  and then  $Et_2CO_3$  gives mainly products of ketonic self-condensation. R. S. C.

**Synthetic differential growth inhibitor.**—See A., 1943, III, 256.

**Syntheses of ethylene  $\alpha\beta$ -disubacate and glyceryl  $\alpha\beta\gamma$ -trisubacate. Metabolic experiments with ethylene  $\alpha\beta$ -disubacate and sebacic acid.** B. Flaschenträger and R. Allemann (*Annalen*, 1942, 552, 106—112).—Freshly distilled  $(CH_2 \cdot OH)_2$  and  $\Delta^4$ -undecenoic acid at  $150^\circ/120$  mm. and then at  $155^\circ/120$  mm. give  $H_2O$  and  $C_2H_4$  diundecenoate, (I), b.p.  $200-219^\circ$ /high vac. It is converted by ozonisation in  $EtOAc$  at  $-18^\circ$  and hydrogenation (Pd sponge) followed by oxidation ( $KMnO_4$  in  $COMe_2$  at room temp.) of the ozonide into  $C_2H_4 H_2$  disubacate, m.p.  $92-94^\circ$  [ $Na_2$ ,  $(NH_4)_2$ ,  $Mg$ ,  $Ca$ ,  $Ba$ , and  $Ag_2$  salts]. Glyceryl triundecenoate is similarly transformed into glyceryl  $H_3 \alpha\beta\gamma$ -trisubacate, m.p.  $88-90^\circ$  [ $(NH_4)_3$ ,  $Na_3$ ,  $Mg_{1.5}$ ,  $Ca_{1.5}$ ,  $Ba_{1.5}$ , and  $Ag_3$  salts]. In the dog (I) behaves in the same manner as free sebacic acid. The ester union of (I) is rapidly hydrolysed in the tissue and esters can scarcely participate, even in chain reactions, in the degradation of fats. H. W.

**Formaldehyde synthesis from methane and oxygen atoms.** M. Kuschnerov and A. Schechter (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 32, 560—562; cf. A., 1935, 1087).—Yields of  $CH_2O$  are recorded on  $CH_4$  mixed with 10%  $O_2$  + 90% A obtained by the action of the silent electric discharge. A. T. P.

**Condensation products of acetaldehyde.** E. E. Connolly (*J.C.S.*, 1943, 42).—Crude aldol contains 35% of recoverable  $MeCHO$ , of which 50% can be recovered at room temp., and the rest by distillation with  $C_6H_6$  or passing through a tube at  $100^\circ$ , but when fractionated in a vac. yields mobile aldol, b.p.  $75^\circ/16$  mm., which rapidly polymerises, especially in the presence of electrolytes. [R] of paralldol (supercooled liquid) shows that it is probably cyclic. Crude aldol with 2% of  $H_2SO_4$  yields a viscid polymeride, b.p.  $136^\circ/17$  mm., which with  $NH_2OH \cdot HCl$  (slowly), or when distilled with dil.  $H_2SO_4$ , gives equimol. amounts of  $MeCHO$  and  $CHMe \cdot CH \cdot CHO$ , and may be



A. Li.

**Derivatives of aldol and of crotonaldehyde. IV. Relationships between the monomeric aldol and its dimeric forms.** E. Spath, R. Lorenz, and E. Freund (*Ber.*, 1942, 75, [B], 1029—1039).—Monomeric aldol (I), paralldol (II), and the "viscous dimeric aldol" (III) in  $H_2O$  or aq.  $MeOH$  give with  $NH_2OH$ , *p*- $NO_2 \cdot C_6H_4 \cdot NH \cdot NH_2$ , or *p*- $C_6H_4Br \cdot NH \cdot NH_2$  in approx. equal amount the corresponding derivatives of (I), b.p.  $110-120^\circ$  (bath)/1 Torr, m.p.  $115.5-116^\circ$ , and m.p.  $126-127^\circ$ , respectively. (I) appears to show a pronounced tendency to form non-cryst. derivatives or to lose  $H_2O$ ; thus even in dil. solution at  $20^\circ$  (I) or (II) affords essentially the dimedon derivative of  $CHMe \cdot CH \cdot CHO$ . In  $H_2O$  (I) and (II) ultimately give an equilibrium mixture containing 48% and 69% of (II) in 2.16 and 9.92% solution. At 10 Torr (III) can be depolymerised to (I). In  $H_2O$  (III) gives an immediate mol. wt. somewhat < is required

D 2 (A., II.)

by  $C_8H_{18}O_4$  and this val. diminishes in time to that observed with (II). At  $100^\circ$  (II) and (III) are interconvertible. Probably (II) and (III) are structurally identical but differ sterically. H. W.

**Preparation of higher fatty aldehydes.**—See B., 1943, II, 4.

**Preparation and polymerisation of methyl vinyl ketone.** T. White and R. N. Haward (*J.C.S.*, 1943, 25—31; cf. B., 1938, 1326).— $COMe_2$  (4 mols.) with paraformaldehyde (1 mol.) at pH 8.3—8.5 (with  $MeOH-KOH$ ) at the b.p. yields a product which on distillation with *o*- $C_6H_4(CO_2Bu)_2$  gives  $CH_2Ac \cdot CMe_2 \cdot OH$  (I) (4—5),  $OH \cdot [CH_2]_2 \cdot Ac$  (27—28),  $OH \cdot CH_2 \cdot CAc \cdot CH_2$  (14—15), 1 : 3-dioxanyl-5 isobutenyl ketone (II), b.p.  $90-92^\circ/12$  mm. (2 : 4-dinitrophenylhydrazones, but no oxime or  $NaHSO_3$  derivative) (10—11), and 1 : 3-dioxanyl-5 Me ketone (3—4%). The "3-ketobutanol" of previous workers is a mixture of some of the above. (II) with cold alkaline  $KMnO_4$  yields  $COMe_2$ , and with  $2N-HCl$ ,  $CH_2O$ . (I), or the crude condensation mixture, when distilled with 10% of  $H_3PO_4$ , and the product treated with  $Ac_2O$  and fractionated, yields  $COMe \cdot CH \cdot CH_2$  (III). The rate of polymerisation of (III) in various solvents has been studied. The rapid polymerisation in precipitants, and the discrepancies in the kinetics of polymerisation in  $C_6H_6$ , confirm that chain termination is retarded in liquids which do not dissolve the polymeride. A. Li.

**Polymerisation of keto-alcohols. I. Preparation and mechanism of polymerisation of  $\gamma$ -ketobutyl alcohol.** E. N. Rutovski, A. A. Berlin, and K. Zaborina (*J. Gen. Chem. Russ.*, 1941, 11, 550—558).—Optimum conditions for prep. of  $OH \cdot [CH_2]_2 \cdot COMe$  (I) from  $COMe_2$  and  $CH_2O$  are: pH 8.2—8.4, temp.  $30-35^\circ$ . The pH should be adjusted to 6.8 as soon as possible after completion of the reaction. Velocity of polymerisation rises with temp. from  $50^\circ$  to  $150^\circ$ . With the exception of  $Ac_2O$  neutral and acid catalysts ( $H_2O_2$ ,  $ZnCl_2$ ,  $P_2O_5$ ,  $Bz_2O_2$ ) have only a very small catalytic action. With 1% of  $Na_2O_2$  the polymerisation reaction is completed after 2 hr., and with 1% of NaOH after 20 hr. Alkaline catalysts have no action in the polymerisation of  $OH \cdot CH_2 \cdot CHMe \cdot COMe$ . Refractometric and surface tension studies suggest that at room temp. 83% of (I) is in the enolic form  $OH \cdot CH_2 \cdot CH \cdot CMe \cdot OH$ , and the catalytic action of alkalis is ascribed to their effect in shifting the equilibrium point towards this form. The polymeride obtained in presence of  $Bz_2O_2$  (36 hr. at  $80^\circ$ ) has a higher sintering point ( $240-243^\circ$ ) than when NaOH is used ( $160^\circ$ ); both polymerides are sol. in org. solvents, but not in  $H_2O$ , and are not affected by exposure to light. R. T.

**Preparation of diacetyl.**—See B., 1943, II, 4.

**Manufacture of  $\alpha$ -dimethylaminopropane- $\beta\gamma$ -diol.**—See B., 1943, II, 4.

**Kinetics of amination of organic halogen compounds in liquid ammonia.**—See A., 1943, I, 65.

**Solubilities and compositions of the phospho-12-tungstates of diamino-acids and of proline, glycine, and tryptophan.** D. D. Van Slyke, A. Hiller, and R. T. Dillon (*J. Biol. Chem.*, 1943, 146, 137—157).—Solubilities of the phospho-12-tungstates of arginine (I) ( $A_3P_2 \cdot 8H_2O$ ;  $A = NH_2$ -acid,  $P = H_3PO_4 \cdot 12WO_3$ ), histidine (II) ( $A_3P_2 \cdot 6$  or  $12H_2O$ ), lysine (III) ( $A_3P_2 \cdot 10H_2O$ ), and cystine ( $AP \cdot 6H_2O$ ) and of glycine (IV) ( $A_3P \cdot 5H_2O$ ), proline (V) ( $A_3P \cdot 2.5H_2O$ ), and tryptophan ( $A_3P \cdot 10H_2O$ ), are measured under varying conditions of temp. and concn. of mineral acid, and approx. optimal conditions are recorded for the phosphotungstate separation of the  $(NH_2)_2$ -from the  $NH_2$ -acids in protein hydrolysates. The time required for complete pptn. of phosphotungstate varies inversely with the solubility; at room temp., (I) and (III), which form the least sol. phosphotungstates, reach max. pptn. in a few hr., (II) and *l*-cystine in 48 hr., and (IV) and (V) in 72—96 hr. (II) forms mixed phosphotungstates with (I) and (III), so that when the mol. sum of (I) + (III) is > that of (II), pptn. of (II) is more complete than is indicated by solubility of the isolated phosphotungstates. Solubility effect of derivatives of (I) and (III) on (II) is plotted as a function of the proportion of (II) in the mixture. (II) does not show a similar effect on the solubility of the phosphotungstates of (I) and (III). A. T. P.

**Organic catalysts. XXIV. Aldol condensation in the presence of secondary amino-acids.** W. Langenbeck and G. Borth (*Ber.*, 1942, 75, [B], 951—953).—Sarcosine, *N*-ethylglycine, *N*-methylalanine, and  $NHMe \cdot CHPh \cdot CO_2H$  are excellent accelerators of the transformation of  $MeCHO$  into aldol, crotonaldehyde, and a small proportion of products of higher b.p. *N*-Ethyl- and *N*-benzyl-alanine and  $\alpha$ -methylaminoisobutyric acid are completely inactive. The catalysts retain their activity over long periods. H. W.

***N*-Monochlorocarbamates.** P. Chabrier (*Compt. rend.*, 1942, 214, 362—365; cf. *ibid.*, 1941, 213, 310).—Interaction of  $OR \cdot CO \cdot NCl_2$  and  $OR \cdot CO \cdot NH_2$  affords  $2OR \cdot CO \cdot NHCl$ , which form salts. *Me N-chlorocarbamate*, m.p.  $32^\circ$  ( $NaOEt$  gives the *Na* salt,  $OMe \cdot CO \cdot NNaCl$ , decomp.  $115^\circ$ ; *Ag* salt, decomp.  $40^\circ$ ),  $NHCl \cdot CO_2Et$  (*Na* salt, decomp.  $140^\circ$ ), and  $\beta$ -chloroethyl *N-chlorocarbamate*, m.p.  $42^\circ$  (*Na* salt, decomp.  $75^\circ$ ), are prepared. A. T. P.

**New preparation and properties of carbamidoformic esters.** P. Charrier (*Compt. rend.*, 1942, 214, 495—497).—Alkali salts of

*N*-chlorocarbamates and amides give carbamidoformic esters:  $\text{NCINa}\cdot\text{CO}_2\text{R}' + \text{R}\cdot\text{CO}\cdot\text{NH}_2 \rightarrow \text{NH}_2\cdot\text{CO}_2\text{R}' \text{ (I)} + \text{NCINa}\cdot\text{COR} \text{ (II)}$ ;  $\text{(II)} \rightarrow \text{RNCO} + \text{NaCl}$ ;  $\text{RNCO} + \text{(I)} \rightarrow \text{NHR}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{R}'$ .  $\text{C}_6\text{H}_6$  is a particularly suitable medium but, in some cases, can be replaced by  $\text{H}_2\text{O}$ . EtOH is apt to lead to production of urethanes. Thus nicotinamide affords *Me nicotinylcarbamidoformate*, m.p. 218°, and Et nicotinoylcarbamate, m.p. 85°. The presence of halogen in amide or carbamate is no obstacle to the reaction. Thus  $\text{NHClAc}$  and  $\text{NCINa}\cdot\text{CO}_2\text{Me}$  afford *Me chloromethylcarbamidoformate*, m.p. 168°, and  $\text{NH}_2\text{Bz}$  and  $\text{NCINa}\cdot\text{CO}_2\text{Et}$  give  $\beta$ -chloroethyl phenylcarbamidoformate, m.p. 117.5°. Reaction appears general and the yields are good with simple aliphatic or aromatic amides but mediocre with  $\text{HCO}\cdot\text{NH}_2$ . Alkalis or alkali carbonates hydrolyse the esters and the products when acidified give  $\text{CO}_2$  and monosubstituted carbamides in good yield:  $\text{NHR}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{H} \rightarrow \text{NHR}\cdot\text{CO}\cdot\text{NH}_2 + \text{CO}_2$ .  $\text{NH}_3$  transforms the esters into substituted biurets whilst  $\text{N}_2\text{H}_4$  yields substituted semicarbazides  $\text{NHR}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$  which react readily with aldehydes and ketones. H. W.

**Catalytic hydrogenation of cystine.** K. E. Kavanagh (*J. Amer. Chem. Soc.*, 1942, **64**, 2721).—Cystine is readily hydrogenated to cysteine in 2*N*-HCl in presence of a little Pd deposited on a high-polymeric support (Pd-PVA). R. S. C.

**Behaviour of cystine dimethyl ester dihydrochloride and of cysteine monomethyl ester monohydrochloride in the Sullivan reaction for cysteine and cystine.** M. X. Sullivan, W. C. Hess, and H. W. Howard (*J. Washington Acad. Sci.*, 1942, **32**, 285—287).—The behaviour of cystine  $\text{Me}_2$  ester dihydrochloride (I) and of cysteine  $\text{Me}$  ester monohydrochloride (II), m.p. 137—138.5°, softens at 110—130° (prep. from cysteine hydrochloride and HCl-MeOH at 45° for 10 min., followed by adding to excess of  $\text{Et}_2\text{O}$  at 0°), in the Sullivan reaction is compared with that of cystine (III) and cysteine (IV). (I) and (II) are hydrolysed by NaCN in aq. NaOH to (III) and (IV), respectively. (I) is hydrolysed by 0.1*N*-HCl at room temp. (22 hr.), whereas (II) is not. (I) and (II) are relatively stable in  $\text{H}_2\text{O}$ , and in solutions of low acidity at room temp., (I) is hydrolysed much more slowly than in 0.1*N*-HCl. (I) and (II) have a higher calorific val. than (III) and (IV), respectively, in the Sullivan reaction, when aq. NaCN is used to cleave the disulphide or to act as adjuvant in the cysteine reaction. If NaCN in *N*-NaOH is used, (I) gives approx. the same val. as (III). (II) treated with 0.1% NaCN in 0.8*N*-NaOH gives the same val. as (IV). A. T. P.

**Taurine.** A. A. Goldberg (*J.C.S.*, 1943, 4—5).— $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{SO}_4\text{H}$  with aq.  $\text{Na}_2\text{SO}_3$  at 140° (50 lb. pressure) for 20 hr. yields taurine (62%), which with the appropriate acid chloride (added gradually) in 5*N*-NaOH yields *Na phenylacetamido*-,  $\beta$ -phenylpropionamido-, and *acetylmandelamido-ethanesulphonate*. Median lethal dosages of these for mice are given. A. Li.

**Manufacture of guanidine carbonate.**—See B., 1942, II, 419.

**Preparation of biuret.**—See B., 1942, II, 421.

**Reaction between thioamides and primary amines.** M. J. Schlatter (*J. Amer. Chem. Soc.*, 1942, **64**, 2722).— $\text{CS}(\text{NH}_2)_2$  with  $\text{NH}_2\text{Bu}^a$  at the b.p. gives  $\text{NH}_3$  and *N-n*-butyl-, b.p. 131.5°/5 mm., and with  $\text{CH}_2\text{Ph}\cdot\text{NH}_2$  at 80° gives *N-n*-benzyl-thioacetamide, m.p. 65.1—65.3° (corr.), b.p. 158—162°/2 mm., but with  $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{NH}_2$  at 60—75° gives (?) *di- $\alpha$ - $\beta'$ -hydroxyethyliminoethyl sulphide*, m.p. 101—101.5° (corr.) [picrate, m.p. 95—95.5° (corr.)].  $\text{H}_2\text{S}$  and  $\text{NH}_3$  may also be formed. R. S. C.

**Acylation of acetonitrile by ethyl *n*-butyrate.** Alcoholysis of the resulting keto-nitrile to ethyl *n*-butyrylacetate. B. Abramovitch and C. R. Hauser (*J. Amer. Chem. Soc.*, 1942, **64**, 2720—2721).—Adding  $\text{MeCN}$  and then  $\text{Pr}^a\text{CO}_2\text{Et}$  to  $\text{NaCPh}_3\text{-Et}_2\text{O}$  gives  $\beta$ -keto-*n*-hexonitrile (52%), b.p. 104—105°/11 mm., converted by  $\text{HCl-EtOH}$  into  $\text{COPr}^a\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ . R. S. C.

**Preparation of adiponitrile.**—See B., 1942, II, 417.

## II.—SUGARS AND GLUCOSIDES.

**Preparation of *d*-fructose 1 : 6-diphosphate by means of baker's yeasts.** C. Neuberg and H. Lustig (*J. Amer. Chem. Soc.*, 1942, **64**, 2722—2723).—Fresh baker's yeast converts sucrose in aq.  $\text{NaH}_2\text{PO}_4\text{-NaHCO}_3\text{-Et}_2\text{O}$  into *d*-fructose 1 : 6-diphosphate, isolated as Ca salt. Dried, but not fresh, Fleischmann's yeast is also effective if  $\text{CCl}_4$  is added. R. S. C.

***D*-Galactosan <1, 5> $\beta$ <1, 6>.** R. M. Hann and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 2435—2438).—The structure of *D*-galactosan <1, 5> $\beta$ <1, 6> (I) is confirmed by oxidation by aq.  $\text{HIO}_4$  at 20° to *L'*-oxy-*D*-methylenediglycollic dialdehyde and thence ( $\text{Br-SrCO}_3$ ) *Sr L'*-oxy-*D*-methylenediglycollate, +5 $\text{H}_2\text{O}$ , and by consumption of 2 equivs. of  $\text{Na}_2\text{I}_4\text{O}_7$  to give 0.98  $\text{HCO}_2\text{H}$ . Pyrolysis of  $\alpha$ -lactose and treating the product with  $\text{COMe}_2\text{-CuSO}_4$  gives *L*-glucosan <1, 5> $\beta$ <1, 6> (13%) and 3 : 4-isopropylidene-*D*-galactosan <1, 5> $\beta$ <1, 6> (II) (18%), m.p. 151—152°,  $[\alpha]_D^{20} - 72.9^\circ$ . In  $\text{C}_6\text{H}_5\text{N}$ , (II) gives 3 : 4-isopropylidene-*D*-galactosan <1, 5> $\beta$ <1, 6> 2-acetate, m.p. 136—137°,  $[\alpha]_D^{20} - 51.4^\circ$ , 2-benzoate (III), m.p. 119—

120°,  $[\alpha]_D^{20} + 6.3^\circ$ , and 2-*p*-toluenesulphonate, m.p. 118—119°,  $[\alpha]_D^{20} - 63.7^\circ$ , and in 0.1*N*-HCl gives (I) (91%), m.p. 223—224°,  $[\alpha]_D^{20} - 22.0^\circ$  in  $\text{H}_2\text{O}$ . In  $\text{C}_6\text{H}_5\text{N}$ , (I) gives the 2 : 3 : 4-tribenzoate (IV), m.p. 89—90°,  $[\alpha]_D^{20} + 84.8^\circ$ , and -tri-*p*-toluenesulphonate, m.p. 103—104° (corr.),  $[\alpha]_D^{20} - 51.1^\circ$ . Boiling 20%  $\text{AcOH}$  hydrolyses (III) to *D*-galactosan <1, 5> $\beta$ <1, 6> 2-benzoate, m.p. 164—165°,  $[\alpha]_D^{20} + 47.2^\circ$ , converted by  $\text{BzCl-C}_6\text{H}_5\text{N}$  into (IV), by  $\text{COMe}_2\text{-CuSO}_4$  into (III), and by  $\text{Ac}_2\text{O-C}_6\text{H}_5\text{N}$  at room temp. into the 2-benzoate 3 : 4-di-acetate, m.p. 103—104°,  $[\alpha]_D^{20} + 85.4^\circ$ , or, similarly, 2-benzoate 3 : 4-di-*p*-toluenesulphonate, m.p. 119—120°,  $[\alpha]_D^{20} + 78.0^\circ$ . Unless otherwise stated,  $[\alpha]$  are  $[\alpha]_D^{20}$  in  $\text{CHCl}_3$ . R. S. C.

**Oxidation of sucrose by periodic acid.** P. Fleury and J. Courtois

(*Compt. rend.*, 1942, **214**, 366—368).—Sucrose (I) (1 mol.) and  $\text{HIO}_4$  (3 mols.) at 14° (24 hr.) afford  $\text{HCO}_2\text{H}$  (1 mol.) and the tetraldehyde (I), oxidised by aq. Br to the corresponding tetra-acid, or by Br in  $\text{BaCO}_3$  or  $\text{SrCO}_3$ , followed by pptn. with EtOH from aq. solution, the respective  $\text{Ba}_2$  or  $\text{Sr}_2$  salt. Acid hydrolysis at 100° of the salts affords glyceric, glyoxylic, and hydroxypyruvic acid, thus confirming the constitution assigned to (I). A. T. P.

**Stabilisation of the glycosidic linking by anhydride formation.** B. Helferich and J. Werner (*Ber.*, 1942, **75**, 949—951).—Glycol iodohydrin  $\beta$ -*D*-glucoside (A., 1940, II, 40) is smoothly converted by boiling NaOH into glycol  $\beta$ -*D*-glucoside anhydride (I), m.p. 210—211°,  $[\alpha]_D^{20} + 56.0^\circ$  in  $\text{H}_2\text{O}$  (triacetate, m.p. 125°,  $[\alpha]_D^{20} + 52.6^\circ$  in  $\text{CHCl}_3$ ), also obtained similarly from glycol chlorohydrin  $\beta$ -*D*-glucoside tetra-acetate. (I) is not hydrolysed by emulsin of sweet almonds nor appreciably by boiling with *N*-HCl or *N*- $\text{H}_2\text{SO}_4$  for 16 hr. H. W.

**Synthesis of phenolic glucosides.** T. H. Bemby and G. Powell (*J. Amer. Chem. Soc.*, 1942, **64**, 2419—2420).—The fully acetylated sugar, ArOH, and  $\text{POCl}_3 + 1\%$  of  $\text{H}_2\text{O}$  in boiling  $\text{C}_6\text{H}_6$  give  $\beta$ -phenyl-*D*-glucoside (44%), -galactoside (44%), and -fructoside tetra-acetate (33%); best prepared at room temp.,  $\beta$ -phenyl-*D*-xyloside triacetate (57%),  $\beta$ -1-naphthyl- (58%) and  $\beta$ -2-diphenyl-*D*-glucoside tetra-acetate (35%), m.p. 155—156° (corr.),  $[\alpha]_D^{20} - 56^\circ$  in  $\text{CHCl}_3$ , and thence  $\beta$ -2-diphenyl-*D*-glucoside (90%), m.p. 76—77° (corr.),  $[\alpha]_D^{20} - 42^\circ$  in EtOH. R. S. C.

**Syntheses of natural phloridzin.** G. Zemplén and R. Bognár (*Ber.*, 1942, **75**, [B], 1040—1043).—4-Benzoylphloracetophenone, KOH, and acetobromoglucose in aq.  $\text{COMe}_2$  at room temp. yield 2-*D*-glucosido-4-benzoylphloracetophenone tetra-acetate, m.p. 176—177°,  $[\alpha]_D^{20} - 30.0^\circ$  in  $\text{C}_6\text{H}_5\text{N}$ , condensed with *p*-OH- $\text{C}_6\text{H}_4\cdot\text{CHO}$  and conc. KOH to naringenin-2'-glucoside, m.p. 173—174°, softens at 149°,  $[\alpha]_D^{20} - 20.6^\circ$  in 96% EtOH,  $-8.2^\circ$  in  $\text{C}_6\text{H}_5\text{N}$ ; this is hydrogenated (Pd-C in 96% EtOH) to phloridzin (+2 $\text{H}_2\text{O}$ ), m.p. 108—110° (loss of  $\text{H}_2\text{O}$ ),  $[\alpha]_D^{20} - 51.7^\circ$  in 96% EtOH for the hydrated material. H. W.

**Synthesis of glucohespertin, a hesperitin-7-glucoside.** G. Zemplén and R. Bognár (*Ber.*, 1942, **75**, [B], 1043—1047; cf. Kolle *et al.*, A., 1936, 970).—4-*D*-Glucosidophloracetophenone tetra-acetate, KOH, and isovanillin in aq. EtOH yield hesperetin-4'-glucoside (I) (chalcone form) (+3 $\text{H}_2\text{O}$ ), m.p. ~110—115° (much evolution of  $\text{H}_2\text{O}$ ), changes at 105°,  $[\alpha]_D^{20} - 32.6^\circ$  in  $\text{C}_6\text{H}_5\text{N}$ , anhyd. m.p. ~200—204°, softens at 160° and becomes viscous at 165°, which gives an amorphous acetate. It is transformed by boiling 0.2%  $\text{H}_2\text{SO}_4$  into hesperetin-7-glucoside (flavanone form) (+1 $\text{H}_2\text{O}$ ), m.p. 206°, softens at 190°,  $[\alpha]_D^{20} - 53.9^\circ$ ,  $[\alpha]_D^{20} - 51.9^\circ$  in  $\text{C}_6\text{H}_5\text{N}$ , but some difficultly removable hesperetin is simultaneously produced so that the homogeneous material is best obtained by hydrolysis of neohesperidin. It is converted by  $\text{Ac}_2\text{O-C}_6\text{H}_5\text{N}$  at room temp. into 7-tetra-acetylglucosido-hesperetin diacetate, m.p. 151—152°,  $[\alpha]_D^{20} - 23.7^\circ$  in  $\text{C}_6\text{H}_5\text{N}$ . Hydrogenation (Pd-C in 96% EtOH) of (I) affords 3-hydroxyphloretin-4'-glucoside 4-Me ether (+2 $\text{H}_2\text{O}$ ), m.p. indef. 88—92°, softens at 82°,  $[\alpha]_D^{20} - 59.7^\circ$  in  $\text{C}_6\text{H}_5\text{N}$ , anhyd. m.p. 155—157° softens at 135°, which gives an amorphous acetate and is hydrolysed by boiling 3% HCl to 3-hydroxyphloretin 4-Me ether, m.p. 194—196°. H. W.

**Vinyl ethers of cellulose.** A. E. Favorski, V. I. Ivanov, and Z. I. Kuznetsova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 630—632).—Cellulose (I) and  $\text{C}_2\text{H}_2$  in an autoclave at 120—150° in presence of a catalyst give mono- and di-vinyl ethers; under the conditions, cellulose is unchanged when  $\text{C}_2\text{H}_2$  is replaced by  $\text{N}_2$ . The ethers are partly sol. or insol. in cuprammonium solution, and are hydrolysed to (I) and  $\text{MeCHO}$ . A. T. P.

## III.—HOMOCYCLIC.

**Conversion of cyclopentane hydrocarbons of petroleum into cyclohexane hydrocarbons.** M. B. Turova-Poljak, N. D. Zelinski, and G. R. Hasan-Zade (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 551—554).—cyclopentane hydrocarbons are isomerised to cyclohexane hydrocarbons by 10% of  $\text{AlCl}_3$  at 35° for 15—18 hr.; dehydrogenation then yields the corresponding  $\text{C}_6\text{H}_6$  derivative. Paraffin hydrocarbons in the petroleum are unaffected. The cyclo-

pentane content of petroleum can be determined by dehydrogenation (Pt-C) at 310° before and after treatment with AlCl<sub>3</sub>. Methylcyclopentane affords cyclohexane, and thence C<sub>6</sub>H<sub>6</sub>. A. T. P.

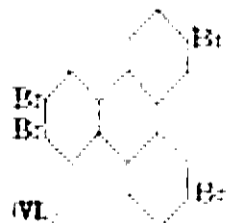
**Reactions of neopentyl systems with electrophilic reagents.** P. Skell and C. R. Hauser (*J. Amer. Chem. Soc.*, 1942, **64**, 2633—2635).—1-hCHO and MgBu<sup>γ</sup>Cl give CHPhBu<sup>γ</sup>OH (I) with some COPhBu<sup>γ</sup>. HBr in light petroleum at 0° gives CHPhBu<sup>γ</sup>Br (II), b.p. 103—104° (corr.)/7.5 mm., which is very slowly hydrolysed by H<sub>2</sub>O, with MeOH-K<sub>2</sub>CO<sub>3</sub> gives the Me ether, b.p. 94—95° (corr.)/20 mm., and with KOAc-AcOH gives the acetate, b.p. 123—124°/16 mm. With aq. AgNO<sub>3</sub> at room temp., (I) gives <70% of (II). CPh<sub>3</sub>-CHPh-OH with HBr-C<sub>6</sub>H<sub>6</sub> or conc. H<sub>2</sub>SO<sub>4</sub> at room temp. gives (CPh<sub>2</sub>)<sub>2</sub>. Differences from the CH<sub>2</sub>Bu<sup>γ</sup> series are as expected. R. S. C.

**Rearrangement of 1:1:3:3:5:5-hexamethylcyclohexane-2:4:6-triol to hexamethylbenzene.** E. B. Ayres and C. R. Hauser (*J. Amer. Chem. Soc.*, 1942, **64**, 2461—2462).—Hexamethylcyclohexane-1:3:5-trione (A., 1940, II, 65) and H<sub>2</sub>-Cu chromite at 200°/200 atm. give 1:1:3:3:5:5-hexamethylcyclohexane-2:4:6-triol, m.p. 251—251.5°, converted by conc. H<sub>2</sub>SO<sub>4</sub> at 0° into C<sub>6</sub>Me<sub>6</sub> (19.4%; very little by 85% H<sub>3</sub>PO<sub>4</sub>; none by SOCl<sub>2</sub>). R. S. C.

**Halogenation of *m*-diphenylbenzene. II. Monoiodo-derivative.** W. A. Cook and K. H. Cook (*J. Amer. Chem. Soc.*, 1942, **64**, 2485—2486).—1:3:4-C<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>Cl with 28% aq. NH<sub>3</sub>-CuCl-CaO-Cu ribbon at 190°/800—850 lb. gives 1:3:4-C<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>NH<sub>2</sub>, m.p. 74° (lit. 64°) (phenylthiocarbamide derivative, m.p. 135°), which by a diazo-reaction (KI) gives 4-iodo-1:3-diphenylbenzene, m.p. 67°, b.p. 235—240° (corr.)/1 mm. R. S. C.

**Separation of anthracene from carbazole.**—See B., 1943, II, 42.

***o*-Terphenyl. II. Derivatives prepared from the hydrocarbon.** C. F. H. Allen and F. P. Pingert (*J. Amer. Chem. Soc.*, 1942, **64**, 2639—2643; cf. A., 1942, II, 355).—*o*- (I) is less reactive than is *m*- or *p*-C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>, but reactions must not be forced to completion lest difficultly separable mixtures be formed. Traces of retained solvents affect the results; e.g., traces of H<sub>2</sub>O or EtOH favour polybromination and AcOH inhibits bromination or nitration. With anhyd. AlCl<sub>3</sub> and BzCl, (I) gives mixtures, but with the additive compound, AlCl<sub>3</sub>.BzCl, in CS<sub>2</sub> gives a good yield of 4'-benzoyl-*o*-terphenyl, *p*-C<sub>6</sub>H<sub>4</sub>Bz-C<sub>6</sub>H<sub>4</sub>Ph-*o*, m.p. 111°, also obtained from *o*-C<sub>6</sub>H<sub>4</sub>PhI by *p*-C<sub>6</sub>H<sub>4</sub>Br-COPh and Cu-bronze at 240° and converted by way of the oxime, forms, m.p. 68° and (stable) 138°, into the anilide and thence 4'-carboxy-*o*-terphenyl (II). With AlCl<sub>3</sub>-Ac<sub>2</sub>O-PhNO<sub>2</sub>, (I) gives 4'-acetyl-*o*-terphenyl (~43%; less by AcCl or in CS<sub>2</sub>), m.p. 94°, also obtained from *o*-C<sub>6</sub>H<sub>4</sub>PhI by *p*-C<sub>6</sub>H<sub>4</sub>Br-COMe and Cu-bronze at 220° and oxidised to (II) by NaOCl. According to the conditions, bromination gives 4':4''-di- (III), m.p. 170°, 4:4':4''-tri- (IV), m.p. 170°, or 4:5:4':4''-tetra-bromo-*o*-terphenyl (V), m.p. 228° (or an isomeride, m.p. 120° after sintering), and finally 3:5:10:11-tetrabromotriphenylene (VI), m.p. >450° (block). Structures are proved by oxidation of (III), (IV), and (V) by CrO<sub>3</sub>-AcOH to *p*-C<sub>6</sub>H<sub>4</sub>Br-CO<sub>2</sub>H, by bromination of (IV) to (V), and by prep. of triphenylene from (VI) by distilling with Zn dust. 1:2:3:6-C<sub>6</sub>H<sub>2</sub>Ph<sub>2</sub>Me<sub>2</sub> gives 4:5:4':5'-tetrabromo-3:6-dimethyl-*o*-terphenyl, m.p. 205°. Conc. HNO<sub>3</sub> in Ac<sub>2</sub>O at 0—5° and later room temp. converts (I) into the 4'-NO<sub>2</sub>- (VII) (78%), m.p. 105—106°, or with less cooling into the 4':4''- (VIII), m.p. 218°, [also obtained from (VII) by fuming HNO<sub>3</sub> in Ac<sub>2</sub>O at 10°—room temp.], and 2':4'-(NO<sub>2</sub>)<sub>2</sub>-compound (IX), m.p. 169°. Oxidation (CrO<sub>3</sub>-AcOH) of (VIII) gives *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>H and of (IX) gives 2:4:1-(NO<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-CO<sub>2</sub>H. H<sub>2</sub>-Raney Ni-EtOH yields 4'-amino-, m.p. 108° (less after keeping) (Bz derivative, m.p. 175°), and 4':4''-diamino-*o*-terphenyl, m.p. 149°, unstable in air, converted by tetra-azo-reactions into (III), (I), and a bis-β-naphtholazo-compound, m.p. 209° (decomp.). Br vapour and (VIII) give 4:5-dibromo-4':4''-dinitro-*o*-terphenyl, m.p. 228°, and some (?) triphenylene derivative. R. S. C.



**New type of condensation reaction under the influence of aluminium chloride.** D. N. Kursanov and R. R. Zelvin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **36**, 17—21).—Contrary to Tzukunftnik *et al.* (A., 1937, II, 331) the condensation product (AlCl<sub>3</sub>) of EtOH with C<sub>6</sub>H<sub>6</sub> has m.p. 179°. This and the product from HCO<sub>2</sub>Et, EtOAc or CH<sub>2</sub>Cl-CO<sub>2</sub>Et with C<sub>6</sub>H<sub>6</sub> and AlCl<sub>3</sub> or PhEt with AlCl<sub>3</sub> is 9:10-dimethylantracene, hydrogenated (Pd-black) to 9:10-dimethyl-1:2:3:4:9:10:11:12-octahydroanthracene, m.p. 140—141.5°. F. R. G.

**Synthesis of naphthalene-2:7-dialdehyde. Attempted synthesis of coronene.** J. H. Wood and J. A. Stanfield (*J. Amer. Chem. Soc.*, 1942, **64**, 2343—2344).—2:7-C<sub>10</sub>H<sub>6</sub>(CN)<sub>2</sub> with SnCl<sub>2</sub>-HCl-Et<sub>2</sub>O and then boiling H<sub>2</sub>O gives naphthalene-2:7-dialdehyde (24.3%), m.p. 142° (corr.) (di-2:4-dinitrophenylhydrazones, decomp. begins at 295°, complete at 312—313°), oxidised by KMnO<sub>4</sub> to 2:7-C<sub>10</sub>H<sub>6</sub>(CO<sub>2</sub>H)<sub>2</sub>. Attempts to obtain coronene from the derived dithioaldehyde (H<sub>2</sub>S-HCl) by Cu and then heat alone or with Se failed. R. S. C.

**Friedel-Crafts acylations of sterically hindered alkylbenzenes.** G. F. Hennion and S. F. deC. McLeese (*J. Amer. Chem. Soc.*, 1942,

**64**, 2421—2422).—*sec*-Alkylbenzenes give (AlCl<sub>3</sub>-CS<sub>2</sub>; -10°) *p*-C<sub>6</sub>H<sub>4</sub>Alk-COMe (I) or *p*-C<sub>6</sub>H<sub>4</sub>Alk-COPh (II). *p*-Di-*sec*-alkylbenzenes give similarly (at the b.p.) 2:5:1-C<sub>6</sub>H<sub>3</sub>Alk<sub>2</sub>-COMe (III) and -C<sub>6</sub>H<sub>3</sub>Alk<sub>2</sub>-COPh (IV). Yields are usually 60—88%. Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub>-AcOH at 65—75° converts (I) or (III) into *p*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>. With boiling HNO<sub>3</sub> (*d* 1.09), (I) gives *p*-C<sub>6</sub>H<sub>4</sub>Alk-CO<sub>2</sub>H, (III) gives 4:1:3-C<sub>6</sub>H<sub>3</sub>Alk(CO<sub>2</sub>H)<sub>2</sub>, (II) gives *p*-C<sub>6</sub>H<sub>4</sub>Bz-CO<sub>2</sub>H, and (IV) gives 2:1:4-C<sub>6</sub>H<sub>3</sub>Bz(CO<sub>2</sub>H)<sub>2</sub>. With CrO<sub>3</sub> and then HNO<sub>3</sub> (1:2; tube), (III; Alk = *sec*-Bu) gives 1:2:4-C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>H)<sub>3</sub>. The following are described. *p*-*sec*-Butyl-, b.p. 134—135°/11 mm. (semicarbazone, m.p. 190—191°), *p*-*sec*-amyl-, b.p. 144—145°/11 mm. (semicarbazone, m.p. 173—174°), *p*-*sec*-octyl-, b.p. 134—135°/3 mm. (semicarbazone, m.p. 144—145°), 2-methyl-5-*sec*-butyl-, b.p. 132—133°/11 mm. (semicarbazone, m.p. 114—115°), 2:5-di-*sec*-butyl-, b.p. 148—149°/14 mm. (semicarbazone, m.p. 160—161°), and 2:5-di-*sec*-amyl-, b.p. 126—127°/3 mm. (semicarbazone, m.p. 149—150°), -acetophenone; *p*-*sec*-butyl-, b.p. 188°/9 mm., *p*-*sec*-amyl-, b.p. 188—190°/5 mm., *p*-*sec*-octyl-, b.p. 212—214°/5 mm., *p*-*sec*-dodecyl-, b.p. 243—245°/4 mm., and 2:5-di-*sec*-butyl-, b.p. 155°/3 mm., -benzophenone; *p*-*sec*-butyl-, m.p. 91—92°, and -amyl-benzoic acid, m.p. 103—104°; 4-*sec*-butyl-, m.p. 237—238°, and -amyl-isophthalic acid, m.p. 230—231°. *p*-C<sub>6</sub>H<sub>4</sub>Bu<sup>γ</sup><sub>2</sub> with AcCl-AlCl<sub>3</sub>-CS<sub>2</sub> gives *p*-C<sub>6</sub>H<sub>4</sub>Bu<sup>γ</sup>-COMe. R. S. C.

**Polymerisation of styrene catalysed by *p*-bromobenzenediazonium hydroxide.** C. C. Price and D. A. Durham (*J. Amer. Chem. Soc.*, 1942, **64**, 2508—2509).—Adding NaOH to *p*-C<sub>6</sub>H<sub>4</sub>Br-N<sub>2</sub>Cl and CH<sub>2</sub>:CHPh in H<sub>2</sub>O at 0° yields a mixed polymeride, containing 4.2% of Br and (from  $\eta$ ) 2 CH<sub>2</sub>:CHPh units; this is due to *p*-C<sub>6</sub>H<sub>4</sub>Br radicals. R. S. C.

**Isomerisation of unsaturated hydrocarbons in presence of oxides of metals. V. Isomerisation of  $\delta$ -phenyl- $\Delta^a$ -butene and  $\epsilon$ -phenyl- $\Delta^a$ -pentene in presence of aluminium and chromium oxide.** R. J. Levina and N. A. Schtscheglova. VI. Isomerisation of  $\delta$ -phenyl- $\Delta^a$ -butene in presence of chromic oxide. R. J. Levina and E. M. Panov (*J. Gen. Chem. Russ.*, 1941, **11**, 527—532, 533—536).—V. Ph-[CH<sub>2</sub>]<sub>2</sub>:CH:CH<sub>2</sub> passed over Al<sub>2</sub>O<sub>3</sub> at 250° or over Cr<sub>2</sub>O<sub>3</sub> at 225° yields CHPh:CH<sub>2</sub>Et. Ph-[CH<sub>2</sub>]<sub>3</sub>:CH:CH<sub>2</sub> yields CHPh:CHPr<sup>a</sup> when passed over Cr<sub>2</sub>O<sub>3</sub> at 250°; with Br in Et<sub>2</sub>O it yields  $\alpha\beta$ -di-bromo- $\epsilon$ -phenylpentane, b.p. 172°/9 mm.

VI. Ph-[CH<sub>2</sub>]<sub>2</sub>:C:CH passed over Cr<sub>2</sub>O<sub>3</sub> at 250° yields CPh:CEt, with a mixture of polymerides. R. T.

**Bromination of diphenylalkanes and preparation of stilbene derivatives. I.  $\alpha\beta$ -Diphenylethane.**—See A., 1943, II, 92..

***s-p*-Dichlorotetraphenylethylene.** C. C. Price and P. E. Fanta (*J. Amer. Chem. Soc.*, 1942, **64**, 2726—2727).—*p*-C<sub>6</sub>H<sub>4</sub>Cl-COPh with PCl<sub>5</sub> at 150° gives *p*-C<sub>6</sub>H<sub>4</sub>Cl-CPhCl<sub>2</sub> (90%), b.p. 189—194°/12 mm., which with NaI-COMe<sub>2</sub> gives a mixture [? COPh-CPh(C<sub>6</sub>H<sub>4</sub>Cl-*p*)<sub>2</sub> + *p*-C<sub>6</sub>H<sub>4</sub>Cl-CO-CPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>Cl-*p*], m.p. 126—145°, but with Zn in dry Et<sub>2</sub>O gives *s*-diphenyldi-*p*-chlorophenylethylene, m.p. 202—203°, reduced by Na-EtOH to (CHPh)<sub>2</sub> and by H<sub>2</sub>-Raney Ni in methylcyclohexane at 100°/110 atm. to a mixture including CPh<sub>2</sub>:CPh-C<sub>6</sub>H<sub>4</sub>Cl-*p*, m.p. 168° (lit. 165—166°, 162°). R. S. C.

**Stereochemistry of diphenylpolyenes.** L. Zechmeister and A. L. LeRosen (*Science*, 1942, **95**, 587—588).—Stereoisomerides of diphenyloctatetraene were prepared by several methods and separated by chromatographic analysis, developing the chromatogram with a C<sub>6</sub>H<sub>6</sub>-light petroleum on Ca(OH)<sub>2</sub>. Preliminary details of the separation are given. E. R. R.

**Isodimorphism of  $\beta$ -naphthol and naphthalene.**—See A., 1943 I, 85.

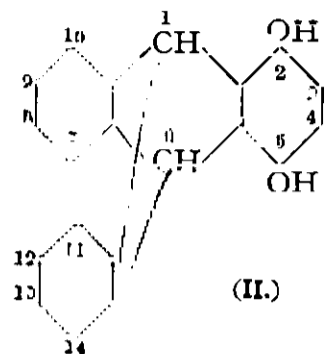
**1:3:5:7-Tetranitronaphthalene and the isomeric tetranitro-derivatives obtained from 2:6-dinitronaphthalene by nitration.** J. Chatt and W. P. Wynne (*J.C.S.*, 1943, 33—36).—Oxidation (HNO<sub>3</sub>, *d* 1.16, at 200°) of 1:3-C<sub>10</sub>H<sub>6</sub>(NO<sub>2</sub>)<sub>2</sub> yields only 3:5:1-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>-CO<sub>2</sub>H, whilst nitration (67% excess of NO<sub>2</sub>:SO<sub>3</sub>H in H<sub>2</sub>SO<sub>4</sub>) gives 1:3:8-C<sub>10</sub>H<sub>5</sub>(NO<sub>2</sub>)<sub>3</sub>. 2:6-C<sub>10</sub>H<sub>6</sub>(NO<sub>2</sub>)<sub>2</sub> {from 2:6-C<sub>10</sub>H<sub>6</sub>(OH)<sub>2</sub> by amination [40% (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> in 20% aq. NH<sub>3</sub> at 140° under pressure], diazotisation, and treatment with NaNO<sub>2</sub> and cuprocupric sulphite} with HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> yields 1:3:5:7- (I), m.p. 260°, decomp. 263—265° (43%), 1:2:6:8- (II), m.p. 138° (8.4%), and ?-tetranitro-naphthalene, m.p. 215° (1.3%). (I) yields with HNO<sub>3</sub> (*d* 1.16) at 200°, 3:5:1-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>-CO<sub>2</sub>H, with POCl<sub>3</sub>-PCl<sub>5</sub> at 180—200°, a mixture of C<sub>10</sub>H<sub>4</sub>Cl<sub>4</sub> and C<sub>10</sub>H<sub>3</sub>Cl<sub>5</sub>, and with SnCl<sub>2</sub> in EtOH-HCl, 1:3:5:7-C<sub>10</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>4</sub>, the hydrochloride of which when diazotised (in H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>) and treated with CO(NH<sub>2</sub>)<sub>2</sub> followed by CuCl in conc. HCl yields a small amount of 1:3:5:7-C<sub>10</sub>H<sub>4</sub>Cl<sub>4</sub> (this could not be repeated). The constitution of (I) is confirmed by m.p. analogy and crystallographic examination. (II) yields with HNO<sub>3</sub> (*d* 1.16) at 190—200°, a mixture of 3:5:1:2-(NO<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> and 3:5:1-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>-CO<sub>2</sub>H, and with PCl<sub>5</sub>-POCl<sub>3</sub> at 180°, a ?-tetrachloronaphthalene, m.p. 125—127°. A. I. I.

**Action of aluminium chloride on tetrahydronaphthalene.** A. Dansi and C. Ferri (*Gazzetta*, 1941, **71**, 648—651).—Tetrahydronaphthalene (I) and AlCl<sub>3</sub> at 35—80° give C<sub>10</sub>H<sub>8</sub>, an oily fraction [dehydrogenated (Se at 350°) to a compound, C<sub>16</sub>H<sub>10</sub>, m.p. 147—

152° (sublimes 180°/2.5 mm.), and a compound,  $C_{20}H_{10}$  (II), m.p. 150.5°, regarded as 1:2:3:4:1':2':3':4'-octahydro-1:2:1':2'-bisanthracene, different from the compound described by von Braun *et al.* (A., 1921, i, 405), and having a similar absorption spectrum to (I). With  $Br-CHCl_3$ , (II) gives a compound,  $C_{20}H_{10}Br$ , m.p. 152°, and with Se at 320–340°, a compound,  $C_{20}H_{12}$ , m.p. 165° (picrate, m.p. 195°), of characteristic absorption spectrum.

E. W. W.

**Triptycene** [9:10-*o*-phenyleneanthracene]. P. D. Bartlett, M. J. Ryan, and S. G. Cohen (*J. Amer. Chem. Soc.*, 1942, **64**, 2649–2653).—The adduct (I), obtained (83%) from anthracene and  $p-O:C_6H_4:O$  in boiling xylene, with 40% HBr (4 drops) in boiling AcOH gives 3':6' (= 1:4)-dihydroxy-9:10-*o*-phenylene-9:10-dihydroanthracene



[2:5-dihydroxytriptycene] (II) (90%), m.p. 338–340° (decomp.), converted by  $H_2$ -Raney Ni in dioxan at 200°/1140 lb. into a  $H_{12}$ -derivative, m.p. 220–224°, which is hydrogenated in the unsubstituted rings and is oxidised by air in aq. alkali. With  $H_2$ -Cu chromite in dioxan at 160°/2200 lb., (I) gives a compound,  $C_{20}H_{20}O_2$ , m.p. 226–228° (diacetate, m.p. 177–178°), stable in air and thus reduced in the quinol ring. Many attempts to remove the OH from (II) failed.

$KBrO_3$ -AcOH- $H_2O$  oxidises (II) to the quinone (93%), m.p. 292–296°, the dioxime, m.p. 246° (decomp.), of which with  $SnCl_2$ -HCl-EtOH at ~60° gives 2:5-diaminotriptycene (III) (86%), m.p. 307° (decomp.) [hydrochloride (IV), decomp. >210°;  $Ac_2$  derivative, decomp. 370°]. Attempts to remove the  $NH_2$  directly from (III) failed. Treating (IV) in AcOH with, successively,  $H_2SO_4$ -AcOH- $H_2O$ ,  $NaNO_2$ , and  $CO(NH_2)_2$  (all at 10°), addition to  $NaH_2PO_2$ -conc. HCl, keeping overnight, and sublimation of the product at 195°/2 mm., gives mono- + a little dichlorotriptycene, m.p. 222–223°, which with  $H_2$ -Pd- $CaCO_3$ - $N_2H_4$ -KOH-EtOH- $H_2O$  gives triptycene [9:10-*o*-phenylene-9:10-dihydroanthracene] (V), m.p. 254.8–255.2°. Treating the tetrazonium solution from (IV) with  $NaH_2PO_2$ -HBr gives a very poor yield of 2:5-dibromotriptycene, m.p. 227–228°, debrominated to (V). Inability of (V) to become planar prevents resonance so that the central CH do not show the same properties as in  $CHPh_3$ . Thus, (V) is unaffected by  $CKPhMe_2$ - $Et_2O$ - $N_2$ ,  $SO_2Cl_2$ - $Bz_2O_2$ , and  $(CH_3CO)_2O$  in boiling  $PhNO_2$ , and is barely affected by  $Cl_2$ - $CCl_4$ ;  $CrO_3$ -AcOH oxidises (V) to anthraquinone (76%) and ~6  $CO_2$ ; this is in accord with bond-fixation (Mills-Nixon effect) since the internal bond-angles are 109° 28'.

R. S. C.

**cyclopentylamides of [aliphatic] carboxylic acids.**—See B., 1943, II, 74.

**Nuclear alkylation of aromatic bases. V. Action of methyl alcohol on *m*-toluidine hydrochloride.** R. W. Cripps and D. H. Hey (*J. C.S.*, 1943, 14–15; cf. A., 1931, 950).— $m-C_6H_4Me \cdot NH_2 \cdot HCl$  (1 mol.) and MeOH (1 mol.) at 210–235° (8 hr.) give *o*-4-xylidine in ~35% yield, with some methylated acridines (I), but no phenols. With 2 or (better) 3 mols. of MeOH at 210–220° (5½ hr.),  $\psi$ -cumidine is formed in ~50% yield, with some (I); 4 mols. of MeOH at 260–280° (10 hr.) afford isoduridine, isodurenol,  $C_6Me_5 \cdot OH$ , and (I). *m*-Methylation in the Hofmann-Martius reaction is established.

A. T. P.

**Compounds of aromatic amines with lower fatty acids.**—See A., 1943, I, 88.

**Sulphonation of benzylethylaniline.** L. Blangey, H. E. Fierz-David, and G. Stamm (*Helv. Chim. Acta*, 1942, **25**, 1162–1179).— $NPhEt \cdot CH_2Ph$  (I) with oleum at >60° gives (cf. Gnehm *et al.*, A., 1908, i, 112) mainly (~78%) *m*-sulphobenzylethylaniline (*K* and *Na* salts; corresponding amide, m.p. 98–99°), which is transformed by nascent Br and subsequent oxidation into *m*- $SO_3H \cdot C_6H_4 \cdot CO_2H$ . In addition ~16% of *p*- and <1% of *o*- $SO_3H \cdot C_6H_4 \cdot CH_2 \cdot NPhEt$  (II) are formed with very little of a disulphonic acid. Excess of  $ClSO_3H$  and (I) give mainly *m*- $SO_2Cl \cdot C_6H_4 \cdot CH_2 \cdot NPhEt$ , whereas use of the calc. quantity of  $ClSO_3H$  in  $PhNO_2$  or application of the "baking" process affords *p*- $SO_3H \cdot C_6H_4 \cdot NEt \cdot CH_2Ph$ . The synthesis of (II) from *o*- $CH_2Br \cdot C_6H_4 \cdot SO_3H$  and  $NPhEt$  is described.

H. W.

**Mixed arylhydroxyalkylamines.**—See B., 1943, II, 74.

**Preparation of diphenylthiocarbazide and diphenylthiocarbazone (dithizone).** O. Grummitt and R. Stickle (*Ind. Eng. Chem. [Anal.]*, 1942, **14**, 953–954).—Improved preps. of diphenylthio-carbazide and -carbazone are recorded.

J. D. R.

**Vinylaryl esters.**—See B., 1943, II, 73.

**Condensation of methylpropylcarbinols with phenol in presence of aluminium chloride.** R. C. Huston and C. R. Meloy (*J. Amer. Chem. Soc.*, 1942, **64**, 2655–2657).— $CMePr^a \cdot OH$ ,  $CMePr^aPr^b \cdot OH$ , and  $CMePr^b \cdot OH$  with  $PhOH-AlCl_3$  at 25–35° give  $\delta$ -*p*-hydroxyphenyl- $\delta$ -methyl-*n*-heptane (65%), m.p. 63–63.5°, b.p. 282–284°/738 mm., 151–152°/6 mm. (3:5-dinitrobenzoate, m.p. 124.5–126°;  $\alpha$ -naphthylurethane, m.p. 105–106°),  $\gamma$ -*p*-hydroxyphenyl- $\beta$ -dimethyl-*n*-hexane (47%), m.p. 72–73°, b.p. 279–281°/738 mm., 122–124°/

2 mm. (3:5-dinitrobenzoate, m.p. 97–98°;  $\alpha$ -naphthylurethane, m.p. 127.5–128.5°), and  $\gamma$ -*p*-hydroxyphenyl- $\beta$ -trimethyl-*n*-pentane (60%), m.p. 57–58.5°, b.p. 275–277°/738 mm., 116–117°/2 mm. (3:5-dinitrobenzoate, m.p. 103–103.5°;  $\alpha$ -naphthylurethane, m.p. 106–107°), respectively. The same compounds are obtained by condensing the carbinols with  $C_6H_6$  and nitrating, reducing, diazotising, and hydrolysing the products (no details).

R. S. C.

**Compound formation between the isomeric hydroxydiphenyls and pyridine.** S. E. Hazlet and R. W. Morrow (*J. Amer. Chem. Soc.*, 1942, **64**, 2625–2628).—F.p. diagrams show that  $C_5H_5N$  with *o*- or *m*- $C_6H_4Ph \cdot OH$  gives stable 1:1 additive compounds, f.p. 38.2° (corr.) or 35.5° (corr.), respectively, but with *p*- $C_6H_4Ph \cdot OH$  gives unstable 1:1 and 1:2 additive compounds.

R. S. C.

**Halogenation of esters in the diphenyl series. II. Chlorination of *p*-diphenyl benzoate and benzenesulphonate.** (Miss) C. M. S. Savoy and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1942, **64**, 2719–2720; cf. A., 1943, II, 28).— $p-C_6H_4Ph \cdot OBz$  with  $Cl_2$  and a trace of I in  $CCl_4$  gives 4'-chloro-4-diphenyl benzoate (55%), m.p. 182°, also obtained by benzylation of  $p-C_6H_4Cl \cdot C_6H_4 \cdot OH$  (I) and hydrolysed to (I) by KOH-EtOH.  $p-C_6H_4Ph \cdot O \cdot SO_2Ph$  gives similarly 4'-chloro-4-diphenyl benzenesulphonate (21%), m.p. 74–75°, similarly obtained from, and hydrolysed to, (I). 2-Chloro-, m.p. 59–60°, 2:6-di-, m.p. 128–129°, and 2:6:4'-tri-chloro-4-diphenyl benzenesulphonate, m.p. 125–126°, are also prepared.

R. S. C.

**Isomorphism of  $\beta$ -naphthol and naphthalene.**—See A., 1943, I, 85.

**Isomerides of stilboestrol. II.** W. H. Linnell and H. S. Shaik-mahamud (*Quart. J. Pharm.*, 1942, **15**, 384–388; cf. A., 1942, II, 9).— $m-C_6H_4Et \cdot OH$  and cold AcOH-Br give 3:4:1- $C_6H_3EtBr \cdot OH$ , b.p. 145–148°/10 mm. (3:5-dinitrobenzoate, m.p. 105–105.5°), methylated ( $Me_2SO_4$ -40% NaOH) to 3:4:1- $C_6H_3EtBr \cdot OMe$ , b.p. 130–132°/15 mm., which did not form a Grignard reagent or Li derivative, and did not give a tolane with  $Ag_2C_2$ .  $m-C_6H_4Et \cdot OMe$  is converted (method: Adams *et al.*, A., 1924, i, 860) into 4:2:1- $OMe \cdot C_6H_3Et \cdot CHO$  (I), b.p. 120–135°/6 mm. (2:4-dinitrophenylhydrazones, m.p. 193–194°; azine, m.p. 110–111°, not convertible into a stilbene by heat), which could not be induced to undergo the benzoin condensation. 4-Methoxy-2-ethylthiobenzaldehyde, m.p. 95–100° (red at 180°) [from (I)-HCl- $H_2S$ -EtOH or (I)- $H_2S$ -EtOH-piperidine], with Cu-bronze at 250° in  $N_2$  gives 4:4'-dimethoxy-2:2'-diethylstilbene (II), m.p. 96–97°, demethylated (MgMeI at 160–170°; poor yield) to the  $(OH)_2$ -derivative (III), m.p. 150°. The oestrogenic activity of (II) and (III) is small (doses of 5 and 1 mg., respectively).

H. B.

**Action of diazo-compounds on quinones. Preparation of diphenyl derivatives.** G. B. Marini-Bettolo (*Gazzetta*, 1941, **71**, 627–635).—2-*p*-Nitrophenyl-1:4-benzoquinone (I) (cf. Kvalnes, A., 1935, 86) is reduced ( $SO_2$ - $H_2O$ ) to 4'-nitro-2:5-dihydroxydiphenyl, m.p. 195° [ $Me_2$  ether (II), m.p. 104°; diacetate, m.p. 115°].  $Sn$ -HCl reduction of (II) gives 4'-amino-2:5-dimethoxydiphenyl, m.p. 145° (hydrochloride, m.p. 225°; picrate, m.p. 184°; 2:5-dimethoxydiphenyl-4'-azoresorcinol, m.p. 105°), converted (diazo-method) into 4'-hydroxy-2:5-dimethoxydiphenyl, m.p. 158°. With  $Ac_2O$ - $H_2SO_4$ , (I) gives 4'-nitro-2:4:5-triacetoxydiphenyl, m.p. 130°. 2-*m*-Nitrophenyl-1:4-benzoquinone (*loc. cit.*) similarly gives 3'-nitro-2:5-dihydroxy-, m.p. 83°, -dimethoxy-, m.p. 84°, and -diacetoxy-, m.p. 100°, 3'-amino-2:5-dimethoxy- (hydrochloride, m.p. 190°; azoresorcinol derivative, m.p. 96°), and 3'-nitro-2:4:5-triacetoxy-diphenyl, m.p. ~60°.  $p-NH_2 \cdot SO_2 \cdot C_6H_4 \cdot N_2Cl$  in aq. NaOAc and benzoquinone in EtOH give 2-phenyl-1:4-benzoquinone-4'-sulphonamide, m.p. 204°.

E. W. W.

**Water-soluble compounds with antihæmorrhagic activity.** B. R. Baker and G. H. Carlson (*J. Amer. Chem. Soc.*, 1942, **64**, 2657–2664).—Data A below are doses in  $\mu g$ . necessary for vitamin-K activity. 1:2:4- $OAc \cdot C_{10}H_5Me \cdot OH$  (I) (A 2), prepared by partial deacetylation of 2:1:4- $C_{10}H_5Me(OAc)_2$  (A., 1942, II, 285), with  $Me_2SO_4$ - $K_2CO_3$ - $COMe_2$  gives 1-acetoxy-4-methoxy-2-methylnaphthalene, m.p. 67–68°, hydrolysed by NaOMe or, better, NaOH- $Na_2S_2O_4$  in aq. MeOH to 4-methoxy-2-methyl-1-naphthol, m.p. 101–103°, which with  $(NH_4)_2SO_3$ - $NH_3$ - $H_2O$  at 175–180° and then  $Ac_2O$ - $C_6H_6$  gives 1-acetamido-4-methoxy-2-methylnaphthalene (II), m.p. 197–199°. 3:1- $C_{10}H_5Me \cdot OH$  (III) (A 5) with  $p-SO_3H \cdot C_6H_4 \cdot N_2Cl$  and then  $Na_2S_2O_4$  gives 4-amino-3-methyl-1-naphthol hydrochloride, chars at 270°, converted by  $K_2Cr_2O_7$  into 1:2:4- $O \cdot C_{10}H_5Me \cdot O$  (A 1) and by  $Ac_2O$ -NaOAc- $H_2O$  at 75° into the *Ac* derivative, m.p. 206–208°. With  $Me_2SO_4$ - $K_2CO_3$ - $COMe_2$  this gives (II), thus proving the orientation of (I) etc. The appropriate naphthol with succinic or glutaric anhydride (IV) in  $C_6H_5N$  at room temp. gives 4-acetoxy-3-methyl-1-naphthyl *H* succinate (A 3), m.p. 136–138°, and glutarate (A 4), m.p. 109–110° (with some di-4-acetoxy-3-methyl-1-naphthyl succinate, m.p. 164–166°), and 3-methyl-1-naphthyl *H* succinate (A 10), m.p. 109–111°. 2:1:4- $C_{10}H_5Me(OH)_2$  (V) (A 1), (IV), and  $NPhMe_2$  in boiling  $CHCl_3$  give 2-methyl-1:4-naphthaquinol di-*(H* glutarate) (A 10), m.p. 156–158°. 4-Acetoxy-3-methyl-1-naphthyl chloroacetate (prep. by  $CH_2Cl \cdot COCl$ - $NPhMe_2$ - $CHCl_3$  at 25° and later the b.p.), m.p. 103.5–104°, is converted by  $NMe_3$ - $COMe_2$  at room temp. into the *N*-trimethylglycinate chloride (A 4), m.p. 217°. 2-

**Methyl-1 : 4-naphthaquinol bischloroacetate** (prep. in  $\text{NPhMe}_2\text{-CHCl}_3$ ), m.p. 109—110°, gives similarly the *di-N-trimethylglycinate dichloride* (A 12),  $+2\text{H}_2\text{O}$ , m.p. 204°. Hydrogenation of 4-acetoxy-3-methyl-1-naphthyl carbobenzyloxy- $\beta$ -alanate [prep. from (I),  $\text{COCl}\cdot[\text{CH}_2]_2\cdot\text{NH}\cdot\text{CO}_2\cdot\text{CH}_2\text{Ph}$ , and  $\text{NPhMe}_2$  in boiling  $\text{CHCl}_3$ ], m.p. 106.5—108°, gives the  $\beta$ -alanate hydrochloride (A 4),  $+ \text{H}_2\text{O}$ , m.p. 164—167°.  $\text{ClSO}_3\text{H}$ ,  $\text{POCl}_3$ , or  $\text{PSCl}_3$  with (I) and  $\text{C}_5\text{H}_5\text{N}$  in  $\text{CCl}_4$  etc. gives Na 4-acetoxy-3-methyl-1-naphthyl sulphate (A 6), the  $\text{Na}_2$  phosphate (A 4),  $+ \text{H}_2\text{O}$ , or  $\text{Na}_2$  thiophosphate (A 10),  $+ \text{H}_2\text{O}$ , respectively. Acetobromoglucose with (I) or (III)— $\text{K}_2\text{CO}_3\text{-COMe}_2\text{-CHCl}_3$  gives 4-acetoxy-3-methyl-1-, m.p. 180—181°, or 3-methyl-1-naphthylglucoside tetra-acetate, m.p. 135—137°, respectively, and thence (hot  $\text{NaOMe-MeOH}$ ) 4-hydroxy-3-methyl-, m.p. 206—208° (A 3), or 3-methyl-1-naphthylglucoside, m.p. 223—225° (A 10), respectively. Acetobromomaltose with (I) or (III) etc. gives 4-acetoxy-3-methyl-, m.p. 183—184°, or 3-methyl-1-naphthylmaltoside hepta-acetate, m.p. 152.5—154°, and 4-hydroxy-3-methyl-, m.p. ( $+ \text{H}_2\text{O}$ ) 145—150° (A 5), or 3-methyl-1-naphthylmaltoside, m.p. 175—178° (A 20), respectively.  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$  in 5 : 1 (vol.)  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  at 100° gives 4-keto-2-methyl-1 : 2 : 3 : 4-tetrahydro-1-naphthoic acid (VI), m.p. 107—110°, decarboxylated by  $\text{CuO}$  in quinoline at 200—215° to 1-keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (VII), b.p. 142—143°/16 mm. (oxime, m.p. 121—122.5°). Heating (VI) with S at 255—265° and then distilling with  $\text{CuO}$  at 1 mm. gives (III), m.p. 88—90°, resolidifies, remelts at 92.5—93°, also obtained from (VII) by Br and then boiling  $\text{NPhMe}_2$ . 2 : 1- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{NO}_2$  with  $\text{H}_2\text{-Raney Ni}$  in  $\text{MeOH}$  at 1—3 atm. gives 2 : 1- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{NH}_2$  [hydrochloride (A 50), new m.p. 228—231° (decomp.)]; Ac derivative (A >50), new m.p. 191—192°, which with  $\delta$ -gluconolactone in 2 : 1  $\text{H}_2\text{O-AcOH-N}_2$  at 100° gives glucono-2-methyl-1-naphthalide (A >50), m.p. 212—214°. 1 : 2- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  with  $\text{H}_2\text{-Raney Ni-NaOH-H}_2\text{O-MeOH}$  at room temp. gives 1-amino-2-naphthylacetic acid (A >200), m.p. 238—240° (decomp.).  $(\text{NH}_4)_2\text{SO}_3\text{-NH}_3\text{-H}_2\text{O}$  with (III) or (V) at 165° gives 3 : 1- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{NH}_2$  [hydrochloride (A >25), m.p. 265—267°] or 2 : 1 : 4- $\text{C}_{10}\text{H}_5\text{Me}(\text{NH}_2)_2$  (VIII) [dihydrochloride (A 3), m.p. 299—301°; Ac derivative (IX), m.p. 308—309°], respectively.  $\text{Na}_2\text{S}_2\text{O}_4\text{-NaOH-H}_2\text{O}$  at 70° or  $\text{SnCl}_2\text{-HCl-H}_2\text{O}$  reduces 1 : 2 : 4- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\text{Me}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H-p}$ , leading to (IX), which is also obtained from 2 : 1- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{NH}_2$  by  $p\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{HSO}_4$  in  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  and then  $\text{H}_2\text{-Pd-C}$  etc. Boiling 1 : 1 (vol.) conc.  $\text{HCl-EtOH}$  hydrolyses (IX) to 4-acetamido-3-methyl-1-naphthylamine, m.p. 190—191° (hydrochloride), also obtained from 4 : 2 : 1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_5\text{Me}\cdot\text{NHAc}$  by  $\text{H}_2\text{-Raney Ni}$  in  $\text{EtOH}$  at room temp., and converted by  $(\text{CH}_2\cdot\text{CO})_2\text{O}$  in hot  $\text{CHCl}_3$  into N-4-acetamido-3-methyl-1-naphthylsuccinamic acid,  $+ \text{AcOH}$  and anhyd., m.p. 250° (decomp. if preheated to 240°), resolidifies, remelts at 269—271°. This is also obtained from (VIII) and  $(\text{CH}_2\cdot\text{CO})_2\text{O}$  by way of N-4-amino-3-methyl-1-naphthylsuccinamic acid (A >50), m.p. 192° (decomp.). 1 : 4-Dimethoxy-2-chloromethylnaphthalene (X) [from 1 : 4- $\text{C}_{10}\text{H}_6(\text{OMe})_2$  (modified prep.; new m.p. 86—87.5°) and  $\text{CH}_2\text{Cl-OMe-AcOH}$  at 25°, m.p. 62—63°, with  $\text{NH}_3\text{-SO}_2\text{-H}_2\text{O}$  at 135° gives impure 1 : 4 : 2- $\text{C}_{10}\text{H}_5(\text{OMe})_2\cdot\text{CH}_2\cdot\text{SO}_3\text{K}$ , oxidised by  $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  at 90—100° to K 2-sulphomethyl-1 : 4-naphthaquinone (A >50) [S-benzylthiuronium salt, m.p. 182—183° (decomp.)]. With boiling  $\text{EtOH-KOH-H}_2\text{S}$  (excess), (X) gives di-1 : 4-dimethoxy-2-naphthylmethyl disulphide, m.p. 116—117°, also obtained by, successively,  $\text{CS}(\text{NH}_2)_2\text{-EtOH}$ ,  $\text{NaOH-aq. EtOH}$ , and  $\text{I-NaOH-H}_2\text{O}$ , and converted by  $\text{H}_2\text{O}_2\text{-AcOH}$  etc. into K and S-benzylthiuronium 3-hydroxy-2-sulphomethyl-1 : 4-naphthaquinone (A >50), m.p. 200—201° (decomp.). Potencies, A, are also recorded as follows : 2 : 1- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{OH}$  5; 2-piperidinomethyl-1-naphthol and 1 : 4- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NHAc}$  >50. The esters of org. acids are too easily hydrolysed to be of use, but those of the inorg. acids are stable even to sterilisation. The glucosides are stable in  $\text{H}_2\text{O}$ , even when sterilised, if air is excluded or reducing agents are present.

R. S. C.

**Acetylenic ethers. III. Halogen derivatives of phenoxyacetylene.** T. L. Jacobs and W. J. Whitcher (*J. Amer. Chem. Soc.*, 1942, 64, 2635—2638; cf. A., 1942, II, 214).—*Ph tri-iodovinyl ether*, m.p. 129—129.5°, is obtained from  $\text{OPh}\cdot\text{C}\cdot\text{MgBr}$  by  $\text{I-Et}_2\text{O}$  or from  $\text{OPh}\cdot\text{C}\cdot\text{CH}$  (I) by  $\text{I-KI-KOH}$ , but only in traces from  $\text{OPh}\cdot\text{C}\cdot\text{Na}$  by I; very unstable liquids (?  $\text{OPh}\cdot\text{C}\cdot\text{Cl}$ ) are also obtained in all cases. Slimmer's  $\text{Br}_2$ -compound, m.p. 29—29.5°, b.p. 117—118°/6 mm. (A., 1903, i, 249), was *Ph  $\beta$ -dibromovinyl ether* (II), since with boiling conc.  $\text{HCl-EtOH-2 : 4 : 1-(NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$  it gives  $[\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot 2 : 4]_2$ , m.p. 311—312° (lit. 326—328°), with  $\text{O}_2\text{-C}_6\text{H}_6$  gives  $\text{OPh}\cdot\text{CHBr}\cdot\text{COBr}$  and thence (KOPh)  $(\text{OPh})_2\text{CH}\cdot\text{CO}_2\text{Ph}$ , and with fuming  $\text{HNO}_3$  at  $-10^\circ$  gives 2 : 4 : 1- $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{OH}$  and 2 : 4 : 6 : 1- $(\text{NO}_2)_3\text{C}_6\text{H}_2\cdot\text{OH}$  [ $\text{OPh}\cdot\text{CBr}\cdot\text{CHBr}$  (III) gives smoothly  $\text{CHBr}_2\cdot\text{CO}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ ]. In ultra-violet light (III) gives an oil (? an isomeride), but (II) is unchanged.  $\text{KOPh-KOH}$  (I) at  $-5^\circ$  to  $-8^\circ$  gives  $\text{OPh}\cdot\text{C}\cdot\text{CBr}$ , a very unstable oil, distillable only at very low pressure and converted by  $\text{Br-CCl}_4$  into  $\text{OPh}\cdot\text{CBr}\cdot\text{CBr}_2$  and by  $\text{Hg}(\text{OAc})_2\text{-HCl-H}_2\text{O-Et}_2\text{O}$  at  $10^\circ$  into  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Ph}$ .

R. S. C.

**$\beta$ -3 : 4-Methylenedioxyphenylisopropylamine.** J. Elks and D. H. Hey (*J.C.S.*, 1943, 15—16).—Piperonal and  $\text{CHBrMe}\cdot\text{CO}_2\text{Et-}$

$\text{NaOEt}$  at room temp., then at 100° (bath), give Et  $\alpha\beta$ -oxido- $\beta$ -3 : 4-methylenedioxyphenyl- $\alpha$ -methylpropionate, b.p. 184—186°/14 mm.; hydrolysis ( $\text{NaOH-90\% aq. EtOH}$ ) and subsequent decarboxylation give 3 : 4-methylenedioxybenzyl Me ketone, b.p. 154—156°/11 mm. This with  $\text{HCO}\cdot\text{NH}_2$  at 160—165°, followed by hydrolysis (dil.  $\text{HCl}$ ), affords  $\beta$ -3 : 4-methylenedioxyphenylisopropylamine, b.p. 138—140°/12 mm. (Ac derivative, m.p. 93°).

A. T. P.

**Derivatives of 4 : 4'-diaminodiphenyl sulphone.**—See B., 1943, III, 63.

**Diaminobenzyl alcohols.**—See B., 1943, II, 74.

**Crystalline vitamin-A.** J. G. Baxter and C. D. Robeson (*J. Amer. Chem. Soc.*, 1942, 64, 2411—2416).—By suitable crystallisation at low temp. vitamin-A forms solvent-free crystals (photomicrograph), m.p. 63—64°, and solvated crystals (A) containing  $\sim 1$  MeOH (photomicrograph), m.p. 7—10°, or  $\sim 1$   $\text{HCO}_2\text{Me}$ , m.p.  $-4^\circ$  to  $2^\circ$  or 7—10°, the solvents being retained at  $<0^\circ$ /high vac. (cf. A., 1938, III, 53; 1939, III, 601; 1940, III, 371). It is uncertain whether (A) are definite compounds. The absorption max. at 328 (? 324) m $\mu$ . has extinction coeff. 1780. The  $\text{SbCl}_3$  colour has an absorption max. at 622 m $\mu$ ., having  $\epsilon_{\text{max}}$  4800; results by the Evelyn photoelectric colorimeter are discussed. The biological potency is  $4.3 \times 10^6$  U.S.P. XI units per g. The mol. wt., elimination max.,  $n$ , Ac and I vals. confirm the accepted structure.

R. S. C.

**Crystalline aliphatic esters of vitamin-A.** J. G. Baxter and C. D. Robeson (*J. Amer. Chem. Soc.*, 1942, 64, 2407—2410).—Vitamin-A and  $\text{RCOCl}$  in  $\text{C}_5\text{H}_5\text{N-(CH}_2\text{Cl)}_2$  give the acetate (I), m.p. 57—58°, palmitate, m.p. 27—28°, and  $\beta$ -naphthoate, m.p. 74—75° (cf. lit.), and divitamin-A succinate, m.p. 76—77°. Extinction coeffs. at 328 m $\mu$ . and of the  $\text{SbCl}_3$  colours at 620 m $\mu$ . are given. The biological potency of all the esters is that calc. (I) is most stable. Photomicrographs are given.

R. S. C.

**Reaction of Grignard reagents with ketone acetals.** R. J. Levina, S. G. Kulikov, and P. G. Parschikov (*J. Gen. Chem. Russ.*, 1941, 11, 567—572).— $\text{CMe}_2(\text{OEt})_2$  with  $\text{MgPhBr}$  yields  $\alpha$ -phenylisopropyl Et ether, b.p. 68°/4 mm., and with  $\text{Mg cyclohexyl bromide}$  gives  $\alpha$ -cyclohexylisopropyl Et ether, b.p. 74—75°/18 mm.; these ethers do not react further with the reagents. trans-, b.p. 134—136°/29 mm., and cis- $\beta$ -ketodecahydronaphthalene  $\text{Et}_2$  acetal, b.p. 132—133°/12 mm., are prepared. cyclohexanone  $\text{Et}_2$  acetal with Grignard reagents affords cyclohexanol and unidentified products.

R. T.

**Malonic ester synthesis and Walden inversion.** W. E. Grigsby, J. Hind, J. Chanley, and F. H. Westheimer (*J. Amer. Chem. Soc.*, 1942, 64, 2606—2610).—Epoxy-cyclopentane (1 mol.) and  $\text{CH}_2(\text{CO}_2\text{Et})_2$  (2 mols.), in boiling  $\text{EtOH-NaOEt}$  (1 mol.) give, with inversion,  $\text{Et}_2$  trans-2-hydroxycyclopentyl-malonate (I) (70—75%; none isolated if 1 mol. of ester is used; 27% in  $\text{C}_6\text{H}_6$ ), b.p. 75°/10 $^{-4}$  mm., hydrolysed by boiling  $\text{N-aq. NaOH}$  (more slowly by more conc. alkali) to the malonic acid (II), m.p. 118.4—118.7° (decomp.; corr.). In boiling  $\text{C}_6\text{H}_5\text{N}$ , (II) gives trans-2-hydroxycyclopentylacetic acid, m.p. 53.3—54.3° (corr.), slowly converted at 160°, as also is (II), into the lactone of cis-2-hydroxycyclopentylacetic acid (unaffected by boiling  $\text{C}_6\text{H}_5\text{N}$ ). (I) is slowly decomposed by  $\text{NaOEt-EtOH}$ . Its formation is discussed.

R. S. C.

**Constitution of o-carboxylic acids in solution.**—See A., 1943, I, 80.

**Complex formation of boric acid with salicylic acid in aqueous solution.** Salts of monosalicylboric acid.—See A., 1943, I, 92, 95.

**Salicylamide. Ammonolysis of methyl salicylate.** E. R. Kline (*J. Chem. Educ.*, 1942, 19, 332).—Details for the ammonolysis on a laboratory scale are given.

L. S. T.

**Hydroxylamine derivatives of anthranilic acid.** A. W. Scott and B. L. Wood, jun. (*J. Org. Chem.*, 1942, 7, 508—516).—The compound obtained from isatoic anhydride by Meyer *et al.* (A., 1886, 358) is not o-aminobenzhydroxamic acid (I) but O-o-aminobenzoylhydroxylamine (II) (cf. Pope, *Diss., Univ. of Georgia*, 1941). It is converted by  $\text{Bz}_2\text{O}$  at  $\sim 70^\circ$  into the Bz derivative, m.p. 157°, which, like (II), does not give the  $\text{FeCl}_3$  test until it has been warmed with  $\text{NaOH}$ . This with  $\text{KOBu}^t$  in  $\text{Bu}^t\text{OH}$  affords a K salt which rearranges in hot  $\text{H}_2\text{O}$  to 2 : 4-diketo-3-phenyltetrahydroquinazoline, m.p. 280°, and o- $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , m.p. 182°. (I), m.p. 149°, obtained from o- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$  and  $\text{NH}_2\text{OH}$ , is fairly stable up to 140° and gives a marked test for hydroxamic acid with  $\text{FeCl}_3$ ; the dry Na salt passes when heated into 2-hydroxybenzimidazole (III), m.p. 302—303°. (I) (as Na salt) is converted by  $\text{BzCl}$  in dioxan into the  $\text{Bz}_2$  derivative, m.p. 169°, the K salt of which rearranges to (III) in boiling  $\text{H}_2\text{O}$ .

H. W.

**$\alpha$ -Arylphthalides.**—See B., 1943, II, 75.

**Carvacrolphthalein.** M. H. Hubacher (*J. Amer. Chem. Soc.*, 1942, 64, 2538—2539).—Carvacrol (I), o- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ , and  $\text{SnCl}_4$  at 100° give carvacrolphthalein (II) (8%; traces by  $\text{ZnCl}_2$ ), m.p. 293.5—294.7° [diacetate, m.p. 217.8—219.7°;  $\text{Me}_2$  ether, m.p. (partial) 202°, resolidifies, remelts at 211.5—212.2°]. Ehrlich's compound (G.P. 225,983; B., 1910, 1474) was thymolphthalein (III) (similarly pre-

pared in 62—70% yield), new m.p. 252.4—253.1° (diacetate, m.p. 153.0—153.6°; Me<sub>2</sub> ether, m.p. 175.9—176.7°), since this is obtained from impure (I). M.p. are corr. (II) and (III) are not laxative to *Rhesus* monkeys. R. S. C.

**Synthesis of 4-hydroxy-2-naphthoic acids.** R. D. Haworth, B. Jones, and Y. M. Way (*J.C.S.*, 1943, 10—13).—Et<sub>2</sub> α-aceto-α-benzylsuccinate [from CH<sub>2</sub>PhCl and CO<sub>2</sub>Et·CH<sub>2</sub>·CNaAc·CO<sub>2</sub>Et in PhMe at 120—130° (bath)] is hydrolysed (2N-NaOH) to benzylsuccinic acid, the anhydride (prep. by cold AcCl), m.p. 95—97° (lit. 102°), of which with AlCl<sub>3</sub>-PhNO<sub>2</sub> gives 4-keto-1:2:3:4-tetrahydro-2-naphthoic acid, m.p. 145—147°, converted by Br-CHCl<sub>3</sub> into its 3-Br-derivative, m.p. 177—180°, and thence [NPhEt<sub>2</sub> at 100° (bath)] into 4:2-OH·C<sub>10</sub>H<sub>6</sub>·CO<sub>2</sub>H (I), m.p. 220—222°. Similarly prepared are *p*-methylbenzylsuccinic acid, m.p. 112—115° (anhydride, m.p. 88.5°), 4-keto-6-methyl-1:2:3:4-tetrahydro-2-naphthoic acid, m.p. 205—207° (3-Br-derivative, m.p. 167—168°), and 4-hydroxy-6-methyl-2-naphthoic acid (11% yield), m.p. 240—241°; *p*-methoxybenzylsuccinic acid, m.p. 100—101° (anhydride, m.p. 92—93°), 4-keto-6-methoxy-1:2:3:4-tetrahydro-2-naphthoic acid, m.p. 151° (3-Br-derivative, m.p. 171°), and 4-hydroxy-6-methoxy-2-naphthoic acid, m.p. 238—239°; *m*-chlorobenzylsuccinic acid, m.p. 125—127° (anhydride, m.p. 75.5°), 7-chloro-4-keto-1:2:3:4-tetrahydro-2-naphthoic acid, m.p. 190—191° (3-Br-derivative, m.p. 180—184°), and 7-chloro-4-hydroxy-2-naphthoic acid, m.p. 285—287° (some 6:1-C<sub>10</sub>H<sub>6</sub>Cl·OH is formed also) (Me ester, m.p. 218—220°; Me ether, m.p. 251—258°), oxidised by KMnO<sub>4</sub>-aq. NaHCO<sub>3</sub> to 4:1:2-C<sub>6</sub>H<sub>3</sub>Cl(CO<sub>2</sub>H)<sub>2</sub>. 3-Bromo-4-keto-1-phenyl-1:2:3:4-tetrahydro-2-naphthoic acid, m.p. 199—202°, affords 4:1:2-OH·C<sub>10</sub>H<sub>5</sub>Ph·CO<sub>2</sub>H (+ some 4:1-C<sub>10</sub>H<sub>5</sub>Ph·OH). Phenylmethylitaconic acid, m.p. 125—140° [probably a mixture of isomerides from CPhMe, (CH<sub>2</sub>·CO<sub>2</sub>Et)<sub>2</sub>, and NaOEt], is converted by boiling AcCl, followed by AlCl<sub>3</sub>-PhNO<sub>2</sub> at 0°, into (probably) 3-methylindenone-2-acetic acid, m.p. 125—145°, and 4-hydroxy-1-methyl-2-naphthoic acid (15—20%), m.p. 203—207° [Me, m.p. 171—174°, and Et ester, m.p. 127—129°; Me ether, m.p. 158—160° (Me ester, m.p. 99.5°)]. *o*-C<sub>6</sub>H<sub>4</sub>Me·COMe, Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and cold EtOH-NaOEt give (after hydrolysis) *o*-toluoylpyruvic acid, m.p. 118°, but conditions for conversion into (I) are not established. Colours of azo-dyes derived from RN<sub>2</sub>Cl and the above acids are given. PhN<sub>2</sub>Cl and (I) in aq. NaOH afford an azo-dye (mixture), hydrogenation (Pd-C, EtOH) and subsequent oxidation (FeCl<sub>3</sub>-aq. HCl) of which yields naphthaquinonecarboxylic acids, m.p. 153—160° (decomp.), decarboxylated to 1:4-naphthaquinone (proving initial coupling at C<sub>1</sub>) and a product, m.p. 130—150°. A. T. P.

**Reaction of furoic acid with tetrahydronaphthalene.** C. C. Price and N. C. Deno (*J. Amer. Chem. Soc.*, 1942, 64, 2601—2602).—Tetrahydronaphthalene, furoic acid (I), and AlCl<sub>3</sub> give *s*-octahydro-1-anthracene (II) (6.3%), m.p. 153—153.5° [(? 9:10)-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 230—235°], and -1-phenanthroic acid (0.25%), m.p. 143—143.5°. With Cu chromite in quinoline at 235°, (II) gives 1:2:3:4-tetrahydroanthracene and anthracene, but with S at 180—190° gives a substance, m.p. 216—226°. C<sub>10</sub>H<sub>8</sub>, (I), and AlCl<sub>3</sub> give neutral, amorphous products. R. S. C.

**Syntheses in the hydroaromatic series. VII. Preparation of partly hydrogenated derivatives of 7-methoxyphenanthrene-2-carboxylic acid and of 7-methoxy-2-acetophenanthrene.** E. Dane and O. Hoss (*Annalen*, 1942, 552, 113—125; cf. A., 1939, II, 429).—7-Methoxy-9:10-dihydrophenanthrene-2-carboxyl chloride (I), b.p. 208—210°/0.025 mm., is transformed successively into 2-diazoaceto-, m.p. 149° (decomp.), 2-chloroaceto- (II), m.p. 117°, and 2-aceto-7-methoxy-9:10-dihydrophenanthrene (III), m.p. 133°. (III) is hydrolysed by HBr (*d* 1.48) in boiling AcOH to 7-hydroxy-2-aceto- (IV), m.p. 188—189°, and (II) is transformed by prolonged hydrogenation (Pd-BaSO<sub>4</sub>) into 7-methoxy-2-*α*-hydroxyethyl- (V), m.p. 116—117°, -9:10-dihydrophenanthrene. Alternatively (I) is converted by ZnMe<sub>2</sub> in PhMe and CO<sub>2</sub> at room temp. into (III), which with NaOEt and HCO<sub>2</sub>Et in Et<sub>2</sub>O-dioxan gives the corresponding CH(OH): derivative, m.p. 136—137°. (III), (IV), and (V) are physiologically inactive. 6-Methoxy-1-acetylenyl-3:4-dihydronaphthalene (VI) and CH<sub>2</sub>:CH·CO<sub>2</sub>H in HBr-Et<sub>2</sub>O at room temp. yield 7-methoxytetrahydrophenanthrene-2-carboxylic acid (VII), m.p. 210—216° (slight decomp.); the Me ester, m.p. 92°, is dehydrogenated by *p*-O:C<sub>6</sub>H<sub>4</sub>:O in PhOMe at 152° to Me 7-methoxydihydrophenanthrene-2-carboxylate, m.p. 85°, and in absence of solvent at 200—220° into Me 7-methoxyphenanthrene-2-carboxylate (VIII), m.p. 134°. (VII) is transformed by SOCl<sub>2</sub> and C<sub>5</sub>H<sub>5</sub>N in PhMe into the chloride, which with CH<sub>2</sub>N<sub>2</sub> in Et<sub>2</sub>O affords 7-methoxy-2-diazoaceto-tetrahydrophenanthrene (IX), m.p. 148° (decomp.), with a 1:1 adduct, m.p. 159° (decomp.), of (IX) and CH<sub>2</sub>N<sub>2</sub>. (IX) gives the corresponding CH<sub>2</sub>Cl ketone, m.p. 132°, attempted hydrogenation (Pd-BaSO<sub>4</sub> in MeOH containing CaCO<sub>3</sub>) of which gave (III) and (V). (VII) is hydrogenated (Pd-C in PhOMe) to 7-methoxyoctahydrophenanthrene-2-carboxylic acid converted by the usual sequence of reactions into 7-methoxy-2-chloroaceto-octahydrophenanthrene, m.p. 99°, reduced to the corresponding, non-cryst., Cl-free ketone which is hydrolysed to 7-hydroxy-2-aceto-octahydrophenanthrene, m.p. 158—159°. Regulated hydrogenation (Pd-CaCO<sub>3</sub> in stable cyclohexane)

of (VI) and treatment of the vinyl derivative produced with CH<sub>2</sub>:CH·CO<sub>2</sub>H at 100° gives 7-methoxyhexahydrophenanthrene-2-carboxylic acid, m.p. 185°, which appears to yield 7-methoxyphenanthrene, m.p. 99°, when heated with Se at 300—320°. The non-cryst. Me ester is dehydrogenated by *p*-O:C<sub>6</sub>H<sub>4</sub>:O in PhOMe to a Me methoxytetrahydrophenanthrenecarboxylate, m.p. 107°, and further by Pd at 250—260° and then at 300° to (VIII). H. W.

**α-Hydroxy-α'-*p*-bromophenylmaleimide.** G. S. Skinner, C. A. Coghlan, and A. S. Berlin (*J. Amer. Chem. Soc.*, 1942, 64, 2600—2601).—Adding Br and H<sub>2</sub>O to CN·CHPh·CO·CO<sub>2</sub>R [reacting as CN·CPh·C(OH)·CO<sub>2</sub>R] (R = Et, Me, or Bu<sup>a</sup>) in CHCl<sub>3</sub> at 45—50° gives an additive compound, which at ~50° loses HBr, rearranges, and cyclises to α-hydroxy-α'-*p*-bromophenylmaleimide (I), m.p. 239—240°, which in hot aq. Na<sub>2</sub>CO<sub>3</sub> gives a Na salt (II), decomp. 321°. Omission of the H<sub>2</sub>O leads to less (I) and some ? C<sub>6</sub>H<sub>4</sub>Br·CH<sub>2</sub>·CN. With CH<sub>2</sub>PhCl, (II) gives the N-CH<sub>2</sub>Ph derivative, m.p. 169—170°, or with AgX gives the unstable Ag salt, converted by EtI-Et<sub>2</sub>O into the N-Et derivative, m.p. 191—192°. Boiling HNO<sub>3</sub>-H<sub>2</sub>O or KMnO<sub>4</sub>-NaHCO<sub>3</sub>-H<sub>2</sub>O oxidises (I) to *p*-C<sub>6</sub>H<sub>4</sub>Br·CO<sub>2</sub>H. Aq. NaOH at room temp. slowly hydrolyses (I) to *p*-C<sub>6</sub>H<sub>4</sub>Br·CH<sub>2</sub>·CO<sub>2</sub>H, NH<sub>3</sub>, and Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. (I) is also obtained from α-hydroxy-α'-phenylmaleimide by Br in PhNO<sub>2</sub> at room temp. R. S. C.

**dl- and meso-γγ'-Diphenyl-γγ'-suberodilactone.** C. C. Price and A. J. Tomisek (*J. Amer. Chem. Soc.*, 1942, 64, 2727).—COPh[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H and Zn dust in boiling 80—90% AcOH give γ-phenyl-γ-butyrolactone (30—40%) and γγ'-diphenyl-γγ'-suberodilactones, m.p. 267° (9%) and 165° (clear at 175.5°) (6%). R. S. C.

**Bromination of diphenylalkanes and preparation of stilbene derivatives. I. αβ-Diphenylethane.** S. Bance, H. J. Barber, and A. M. Woolman (*J.C.S.*, 1943, 1—4).—(CH<sub>2</sub>Ph)<sub>2</sub> and Br (excess) in boiling CCl<sub>4</sub> give (CHPhBr)<sub>2</sub>, which could not be further brominated; in boiling H<sub>2</sub>O-AcOH, a mixture of 2:4': αβ-tetrabromo-αβ-diphenylethane (I), m.p. 170—175°, and the 4:4': αβ-isomeride (II) [also obtained from (*p*-C<sub>6</sub>H<sub>4</sub>Br·CH<sub>2</sub>)<sub>2</sub> and Br in boiling CHCl<sub>3</sub> or AcOH] results, but gradual addition of the Br gives a product containing <4 Br per mol. (II) with CuCl or CuCN (2 mols.) in boiling C<sub>5</sub>H<sub>5</sub>N yields 4:4'-dibromo-, converted by CuCN in C<sub>5</sub>H<sub>5</sub>N at 220° (bath) into 4:4'-dicyano-stilbene (III), also obtained from (II) and CuCN (4 mols.) in C<sub>5</sub>H<sub>5</sub>N at 200—210°. (II) in EtOH with MeOH-KOH affords 4:4': α-tribromostilbene, m.p. 82—83°. (III) with Br in PhNO<sub>2</sub> at 200° in bright light yields αβ-dibromo-4:4'-dicyano-αβ-diphenylethane (IV), m.p. 269° (decomp.), which with MeOH-KOH gives α-bromo-4:4'-dicyanostilbene, m.p. 144—145° (130—132° after melting, supercooling, and remelting). This or (better) (IV) with EtOH-MeOH-KOH yields 4:4'-dicyanotolane (V), m.p. 252—255°, reduced (H<sub>2</sub>, Raney Ni in dioxan) to cis-4:4'-dicyano-, m.p. 152—154° [gives the *trans*-compound in boiling PhNO<sub>2</sub>-I (trace)], converted via the imino-ether into cis-4:4'-diamidinotolane (+H<sub>2</sub>O), m.p. 204—206° (decomp.). 4:4'-Diamidinotolane dihydrochloride (+0.5 H<sub>2</sub>O) is prepared from (V). Residues from crystallisation of (III) when sublimed at 250°/1 mm. yield 4-bromo-4'-cyanostilbene, m.p. 187—188°. (I) with CuCl in C<sub>5</sub>H<sub>5</sub>N yields 2:4'-dibromostilbene, m.p. 84—85°, oxidised (KMnO<sub>4</sub> in 80% CMe<sub>2</sub>) to *o*- and *p*-C<sub>6</sub>H<sub>4</sub>Br·CO<sub>2</sub>H. (I) with CuCN (4 mols.) in C<sub>5</sub>H<sub>5</sub>N yields 2:4'-dicyanostilbene, m.p. 136—137°. 2-Cyano-4'-amidinostilbene has m.p. 200—205° (decomp.); the diamidine could not be obtained by the NaNH<sub>2</sub> method. A. Li.

**Formation of diethyl cyclobutane-1:1-dicarboxylate by the Kishner process.** V. P. Golmov and B. A. Kazanski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 37—40).—Cl·[CH<sub>2</sub>]<sub>3</sub>·Br (I) and CHNa(CO<sub>2</sub>Et)<sub>2</sub> in boiling EtOH, or (I)-CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>-Et<sub>2</sub>O-NaOEt-EtOH at room temp., give Cl·[CH<sub>2</sub>]<sub>3</sub>·CH(CO<sub>2</sub>Et)<sub>2</sub> (II) (52%), some (Cl·[CH<sub>2</sub>]<sub>3</sub>)<sub>2</sub>C(CO<sub>2</sub>Et)<sub>2</sub> and [CH<sub>2</sub>]<sub>3</sub>[CH(CO<sub>2</sub>Et)<sub>2</sub>]<sub>2</sub>. (II) is the intermediate in the Kishner reaction, and is convertible by boiling EtOH-NaOEt into Et<sub>2</sub> cyclobutane-1:1-dicarboxylate. A. T. P.

**cycloButane derivatives. III. cis-cycloButane-1:3-dicarboxylic acid.** E. R. Buchman, A. O. Reims, and M. J. Schlatter (*J. Amer. Chem. Soc.*, 1942, 64, 2703—2705).—Distillation at 2 mm. of the mixed anhydride from *trans*-cyclobutane-1:3-dicarboxylic acid (I) or its Ag salt and boiling AcCl gives the anhydride, m.p. 47.5—48°, of, and thence (evaporation with 6N-HCl), *cis*-cyclobutane-1:3-dicarboxylic acid (II), m.p. 143—143.5° (cf. *J.C.S.*, 1898, 73, 330). With MeOH-H<sub>2</sub>SO<sub>4</sub>, (II) gives the Me<sub>2</sub> ester (III), b.p. 110—111°/20 mm., and thence the dihydrazide, m.p. 172—174°. The di-*p*-bromophenacyl ester (prep. from the Na<sub>2</sub> salt) has m.p. 121.2—121.7°. (II) is largely carbonised by conc. HCl at 180° and at 200° alone gives only its anhydride. (I) is obtained from (III) by boiling MeOH-NaOMe, followed by hydrolysis (evaporation with 6N-HCl), CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> and 40% CH<sub>2</sub>O, best with a little piperidine at 0° (later room temp.), give, after hydrolysis (NaOH-MeOH at 0° and later room temp.) and boiling with HCl, CO<sub>2</sub>H·C(CH<sub>2</sub>)<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H (IV) (20%), m.p. 131—132°, b.p. 175°/3.5 mm., a substance, C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>NCl, m.p. 220—220.5°, CO<sub>2</sub>H·[CH<sub>2</sub>]<sub>3</sub>·CO<sub>2</sub>H, pentane-*α*-γ-tricarboxylic acid, and *αα'*-dimethyleneglutaric acid, m.p. 152—153° (cf. *J.C.S.*, 1900, 77, 294; 1908, 93, 1777; 1909, 95, 1166). (II)

and (IV) are distinguishable by resistance of (II) to, and oxidation of (IV) by,  $\text{KMnO}_4$  and by ready addition of  $\text{HBr}$  or  $\text{CH}_2\text{N}_2$  to (IV) ( $\text{CH}_2\text{N}_2\text{--Et}_2\text{O}$  and then  $\text{NH}_3\text{--EtOH}$  at  $100^\circ$  give the *pyrazoline-diamide*,  $\text{C}_7\text{H}_{12}\text{O}_2\text{N}_4$ , m.p.  $145\text{--}145.5^\circ$ ).  $\text{HCl--EtOH}$  largely polymerises (IV) but gives also 43% of  $\text{Et}_2$  ester, b.p.  $132\text{--}133^\circ/23$  mm., which yields no cryst. dihydrazide; the *anhydride* has m.p.  $51\text{--}51.5^\circ$ , b.p.  $112\text{--}115^\circ/2$  mm.; the dichloride ( $\text{SOCl}_2$ ), b.p.  $82\text{--}83^\circ/5$  mm., gives the *diamide*, m.p.  $164\text{--}165^\circ$ ; the *di-p-bromophenacyl* ester has m.p.  $121.6\text{--}121.7^\circ$ . M.p. are corr. R. S. C.

**Chemical components of the roots of *Decalepis hamiltonii*. V. 4-Methylresorcyraldehyde as preservative.**—See A., 1943, III, 294.

**Gossypol. II. Anilino-derivatives. III. Methylation.** K. S. Murty and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, A, 16, 141—145, 146—150).—II. With excess of  $\text{NH}_2\text{Ph}$ , gossypol (I) forms "*tetra-anilinogossypol*" (II), m.p.  $303^\circ$  (decomp.) [probably results from the change  $2\text{CHO} \rightarrow 2\text{CH}(\text{NHPH})_2$ ], which decomposes on heating for a long time at  $110^\circ$  or for a short period at  $180^\circ$  into  $\text{NH}_2\text{Ph}$  and gossypoldianil (III), m.p.  $303^\circ$  (decomp.). (I) and  $\text{NH}_2\text{Ph}$  (2 mols.) in  $\text{Et}_2\text{O}$  give the impure additive compound,  $[2\text{CHO} \rightarrow 2\text{CH}(\text{OH})\cdot\text{NHPH}]$ , m.p.  $303^\circ$  (decomp.). Acetylation and methylation of (II) or (III) yield only derivatives of (I),  $\text{NH}_2\text{Ph}$  being removed.

III. Adams' method (A., 1938, II, 452) of methylating (I) does not appear to give a homogeneous  $\text{Me}_6$  ether (II), m.p.  $130^\circ$ , which is obtained from gossypol hexa-acetate with  $\text{Me}_2\text{SO}_4$  and alkali in  $\text{COMe}_2$ , from (I) and  $\text{CH}_2\text{N}_2$  in  $\text{MeOH}$ , or  $\text{MeI}$  and  $\text{K}_2\text{CO}_3$  in  $\text{COMe}_2$ , or  $\text{Me}_2\text{SO}_4$  and alkali. The methods which do not employ alkali hydroxide give less coloured products. (II) is unaffected by hot dil.  $\text{H}_2\text{SO}_4$  and hence does not appear to have the constitution corresponding with the structure of the glycosides. H. W.

**Reductions with nickel-aluminium alloy and aqueous alkali. I. Carbonyl group.** D. Papa, E. Schwenk, and B. Whitman (*J. Org. Chem.*, 1942, 7, 587—590).—The reduction of alkali-sol. CO compounds proceeds smoothly and with good yields with Ni—Al (Raney alloy) whereas alkali-insol. compounds require a solvent, e.g.,  $\text{EtOH}$ ,  $\text{PhMe}$ . Compounds  $\text{COPhR}$ , where  $\text{R} = \text{H}$ , aryl, or alkyl, give the corresponding hydrocarbon, whereas  $\text{Ph}[\text{CH}_2]_x\text{COR}$  or  $\text{CHPh}\cdot\text{CH}[\text{CH}_2]_x\text{COR}$ , where  $\text{R}$  is  $\text{H}$  or alkyl, give generally the corresponding alcohol. *p-γ-Phenylpropylphenoxyacetic acid* has m.p.  $92\text{--}93^\circ$ . H. W.

**Acyloins, di- and poly-ketones. I. Syntheses in the αδ-diphenylbutane series. I.** P. Ruggli and B. Hegedüs (*Helv. Chim. Acta*, 1942, 25, 1285—1296).— $\text{CH}_2\text{Ph}\cdot\text{CHO}$  (prep. from  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  described) is converted through the H sulphite into  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{CN}$  and thence by  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  into αδ-diphenylbutan-β-ol-γ-one (I), m.p.  $52^\circ$  (*p-nitrobenzoate*, m.p.  $83\text{--}84^\circ$ ; *semicarbazone*, m.p.  $167\text{--}169^\circ$ , softens at  $164^\circ$ ). (I) and  $\text{NHPH}\cdot\text{NH}_2$  in boiling 70%  $\text{AcOH}$  give the corresponding *osazone*, m.p.  $172\text{--}174^\circ$ , and *phenylhydrazone*, m.p.  $111\text{--}113^\circ$ . (I) is reduced by Na in boiling  $\text{EtOH}$  to  $[\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})]_2$ , m.p.  $129\text{--}131^\circ$ . (I) is also obtained in small yield by the action of Na powder on  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$ . Reduction of  $\text{CH}_2\text{Ph}\cdot\text{COCl}$  by  $\text{Mg--MgI}_2$  gives a liquid with odour of  $\text{CPh}_2\text{CH}$  [hydrogenated (Raney Ni) to a compound  $\text{C}_8\text{H}_{10}\text{O}$  which could not be caused to react with reagents for  $\cdot\text{OH}$  or  $\cdot\text{CO}$ ], a mixture of compounds, and  $\text{CH}_2\text{Ph}\cdot\text{CO}_2[\text{CH}_2]_2\text{Ph}$ , converted by  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  into  $(\text{CH}_2\text{Ph})_3\text{C}\cdot\text{OH}$ , m.p.  $113\text{--}114^\circ$ . H. W.

**Effect of solvents on the acylation of phenol with acid chlorides of high mol. wt.** A. W. Ralston, A. Ingle, and M. R. McCorkle (*J. Org. Chem.*, 1942, 7, 457—461; cf. A., 1941, II, 66).— $\text{PhNO}_2$  has a much greater *para*-directing influence than  $\text{CS}_2$  on the Friedel-Crafts acylation of  $\text{PhOH}$  with  $\text{C}_n\text{H}_{2n+1}\cdot\text{COCl}$  ( $n = 7, 9, 11, 13, 15$ , and  $17$ ) in presence of an excess of  $\text{AlCl}_3$ . In  $\text{C}_2\text{H}_2\text{Cl}_4$  only resinous products are obtained with chlorides more complex than  $\text{C}_7\text{H}_{15}\cdot\text{COCl}$ . The length of the alkyl chain has little influence on the *o/p* ratio for a given solvent. *o-*, m.p.  $35.0\text{--}35.5^\circ$ , and *p-*, m.p.  $63.5\text{--}64.0^\circ$ , *-hydroxydecophenone* are new. H. W.

**Rearrangement of phenyl octoate with ferric chloride, titanium tetrachloride, stannic chloride, and zinc chloride.** A. W. Ralston, E. W. Segebrecht, and M. R. McCorkle (*J. Org. Chem.*, 1942, 7, 522—527).— $\text{FeCl}_3$  is comparable to  $\text{AlCl}_3$  as catalyst in the rearrangement of  $\text{Ph}$  octoate but gives a greater ratio of *p-* (I) to *o-* (II) *-hydroxyoctophenone* for the same % of ester conversion. When  $\text{FeCl}_3$  is used the (I)/(II) ratio is less as the mol. amount of catalyst increases whereas with  $\text{AlCl}_3$  the reverse is true; (I) and (II) appear unchanged when heated for 6 hr. at  $70^\circ$  with a mol. ratio of  $\text{FeCl}_3$ .  $\text{TiCl}_4$  is less effective than  $\text{FeCl}_3$  and the (I)/(II) ratio is less. Substantial amounts of octoic acid and *p*-octoylphenyl octoate (III) are also produced. With  $\text{TiCl}_4$  and  $\text{PhNO}_2$  as solvent the (I)/(II) ratio exceeds that in  $\text{C}_2\text{H}_2\text{Cl}_4$ ; in  $\text{CS}_2$  the change proceeds less rapidly than in  $\text{C}_2\text{H}_2\text{Cl}_4$  or  $\text{PhNO}_2$ . Rearrangement of (I) or (II) is not caused by  $\text{TiCl}_4$ .  $\text{SnCl}_4$  is a much weaker catalyst than either  $\text{FeCl}_3$  or  $\text{TiCl}_4$ ; even at  $150^\circ$  the yields of (I) and (II) are quite small and a large proportion of ester is recovered unchanged. (III) is produced in notable amount.  $\text{ZnCl}_2$  has only very slight catalytic activity in  $\text{PhNO}_2$  or  $\text{C}_2\text{H}_2\text{Cl}_4$  under conditions varying from 6 hr. at  $100^\circ$  to 24 hr. at  $160^\circ$ . H. W.

**Derivatives of 2-propionyl-1-naphthol.** C. M. Brewster and G. G. Watters (*J. Amer. Chem. Soc.*, 1942, 64, 2578—2580).—1. 2-OH· $\text{C}_{10}\text{H}_7\cdot\text{COEt}$  (I) is best obtained from  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$ ,  $\text{EtCO}_2\text{H}$ , and  $\text{ZnCl}_2$  at  $145\text{--}150^\circ$  or, less well, by displacement of  $\text{Ac}$  from 1:2-OH· $\text{C}_{10}\text{H}_7\cdot\text{COMe}$  (II). With  $\text{BzOH--ZnCl}_2$ , (II) gives a little 1:2-OH· $\text{C}_{10}\text{H}_7\cdot\text{COPh}$ . (I) is triboluminescent, gives an *Et ether*, b.p.  $175\text{--}180^\circ/15$  mm., *phenylhydrazone*, m.p.  $136^\circ$ , 4-*Br-*, m.p.  $98\text{--}99^\circ$  (with  $\text{RBr--NaOH--H}_2\text{O--COMeEt}$  gives an *Et*, m.p.  $68\text{--}69^\circ$  and *Pr<sup>a</sup> ether*, b.p.  $298\text{--}303^\circ/690$  mm., and with  $\alpha\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CHO--KOH--H}_2\text{O--EtOH}$  at  $0^\circ$  gives a  $\alpha\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}$  derivative, m.p.  $129^\circ$ ), an  $\alpha\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}$ , m.p.  $93\text{--}94^\circ$ , and (by  $\text{HNO}_3\text{--AcOH}$ ) 4- $\text{NO}_2$ -derivative, m.p.  $162\text{--}163^\circ$  (*phenylhydrazone*, m.p.  $199\text{--}200^\circ$ ). Clemmensen reduction of (I) gives 2:1- $\text{C}_{10}\text{H}_6\text{Pr}^a\cdot\text{OH}$ , m.p.  $48\text{--}50^\circ$  (*Et*, b.p.  $294\text{--}296^\circ/690$  mm., and *Bu<sup>a</sup> ether*, b.p.  $304\text{--}306^\circ/692$  mm.). R. S. C.

**Study of the mechanism of the Beckmann rearrangement by the isotopic method.** A. E. Brodski and G. P. Mikluchin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 32, 558—559).—Beckmann rearrangement of  $\text{CPh}_2\cdot\text{N}\cdot\text{OH}$  by  $\text{PCl}_5\text{--Et}_2\text{O}$  at  $-15^\circ$ , with subsequent addition of  $\text{H}_2\text{O}$  enriched in  $^{18}\text{O}$ , gives  $\text{NHBzPh}$ , which is hydrogenated ( $\text{MoS}_3$ ) at 90 atm. The *d* of the  $\text{H}_2\text{O}$  obtained after hydrogenation is in accordance with that of the  $\text{H}_2\text{O}$  applied to hydrolysis. Results suggest that the Beckmann change cannot be explained by direct intermol. rearrangement, but that there is an intermediate elimination of O (e.g., as  $\text{H}_2\text{O}$ ), and subsequent rearrangement, possibly within the substituted ammonium ion. A. T. P.

**Study of mechanisms of chemical reactions with oxygen isotopes. II. Beckmann rearrangement.**—See A., 1943, I, 64.

**p-Acylation of polyalkylbenzophenones by aryl 2:4:6-trialkylbenzoates.** R. C. Fuson, E. M. Bottorff, R. E. Foster, and S. B. Speck (*J. Amer. Chem. Soc.*, 1942, 64, 2573—2756).— $\text{COPhM}$  ( $\text{M} =$  mesityl or other highly hindered  $\text{Ph}$ ) and  $\text{MCO}_2\text{Ar}$  in presence of bases, e.g., Na,  $\text{MgEtBr}$ ,  $\text{MgMgBr}$ ,  $\text{Mg} + \text{MgI}_2$ , give  $p\text{-C}_6\text{H}_4(\text{COM})_2$  and  $\text{ArOH}$  (cf. A., 1942, II, 311). *p*-Tolyl mesitoate (I) and  $\text{MgPhBr}$  in  $\text{Bu}^a_2\text{O--N}_2$  at  $100^\circ$  give *p-dimesitoylbenzene* (II) (34%), m.p.  $244\text{--}246^\circ$  [and *p-cresol* (74%); cf. *loc. cit.*], also obtained (44%) by Friedel-Crafts reaction (A) [ $p\text{-C}_6\text{H}_4(\text{COCl})_2$ ,  $s\text{-C}_6\text{H}_3\text{Me}_3$ , and  $\text{AlCl}_3$  in boiling  $\text{CS}_2$ ]. Similarly *m-tolyl mesitoate*, m.p.  $38\text{--}39^\circ$ , and  $\text{MgPhBr}$  give a little (II),  $\alpha\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$  1:2:4:6, and *m-cresol* (80%); (I) with *o*- or *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$  gives 2:5-dimesitoyl-toluene (III) (29 and 11%, respectively), m.p.  $189^\circ$  [(A) gives 29%], and with *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$  gives 2:5-dimesitoylanisole (IV) (3.5%), m.p.  $210^\circ$  [(A) gives 35%]; *p*-tolyl 2:4:6-triisopropyl- and -triethylbenzoate, b.p.  $170\text{--}171^\circ/3$  mm., with  $\text{MgPhBr}$  give *p-di-2:4:6-triisopropyl-* (V), m.p.  $223\text{--}225^\circ$  [(A) gives 50%], and -triethylbenzoylbenzene (VI), m.p.  $119\text{--}120^\circ$  [(A) gives 67%]. 2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{COPh}$  (VII) and (I) with  $\text{Mg} + \text{MgI}_2$  in  $\text{PhMe--Bu}^a_2\text{O--Et}_2\text{O--N}_2$  at  $115^\circ$  give 40% and at  $60^\circ$  give 36% of (II), with a small amount of a compound, m.p.  $189^\circ$ ; use of  $\text{MgEtBr}$  or  $\text{MgPhBr}$  at  $115^\circ$  gives 13—14%, of 2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{MgBr}$  at  $115^\circ$  gives 17%, of Na at  $100^\circ$  gives 8%, but of  $\text{ZnCl}_2$  gives none. *Ph dibromomesityl ketone* [prep. by bromination of (VII); 23%], m.p.  $113^\circ$ , with (I)— $\text{Mg--MgI}_2$  at  $60^\circ$  gives 27% of 1-mesitoyl-4-dibromomesitoylbenzene (27%), m.p.  $274\text{--}277^\circ$ . *m-Tolyl mesityl ketone* [prep. by (A); 91%], m.p.  $67^\circ$ , with (I)— $\text{Mg--MgI}_2$  at  $115^\circ$  gives (III) (32%). *m-OMe·C<sub>6</sub>H<sub>4</sub>·CO·C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>* 1:2:4:6 with (I)— $\text{Mg--MgI}_2$  at  $70^\circ$  gives (IV) (35%). *m-Dimesitoylbenzene* [prep. by (A); 94%], m.p.  $149\text{--}151^\circ$ , with (I)— $\text{Mg--MgI}_2$  at  $115^\circ$  gives 13% of 1:2:4- $\text{C}_6\text{H}_3(\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$  1:2:4:6)<sub>3</sub>. With 2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{Me--Mg--MgI}_2$  at  $115^\circ$ , (VII) gives only  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$ , but with 2:4:6-tribromophenyl mesitoate, m.p.  $86^\circ$ , at  $100^\circ$  gives (II) and 2:4:6:1- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{OH}$ . *Mesityl α-C<sub>10</sub>H<sub>7</sub> ketone* [prep. by (A); 60%], m.p.  $159^\circ$ , with (I)— $\text{Mg--MgI}_2$  at  $115^\circ$  gives 1:4-dimesitoylnaphthalene (VIII) (30%), forms, m.p.  $171^\circ$  and  $193.5^\circ$  (softens at  $171^\circ$ ). *p-Tolyl 2:3:5:6-tetramethylbenzoate*, m.p.  $138^\circ$ , and 2:3:5:6:1- $\text{C}_6\text{H}_4\text{Me}_4\cdot\text{COPh}$  [prep. by (A); 40%], m.p.  $119^\circ$ , with  $\text{Mg--MeI}_2$  at  $60^\circ$  give *p-di-2:3:5:6-tetramethylbenzoylbenzene* (54%), m.p.  $246^\circ$  [(A) gives 67%]. 2:4:6:1- $\text{C}_6\text{H}_2\text{Pr}^3\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\text{Me-p}$  and 2:4:6-triisopropylbenzophenone [prep. by (A); 81%], m.p.  $97\text{--}99^\circ$ , with  $\text{MgEtBr}$  at  $140^\circ$  give a trace of (V). 2:4:6:1- $\text{C}_6\text{H}_2\text{Et}_3\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\text{Me-p}$  and 2:4:6-triethylbenzophenone [prep. by (A); 81%], b.p.  $144\text{--}145^\circ/3$  mm., with  $\text{Mg--MgI}_2$  at  $115^\circ$  give 16% of (VI). Impure 1:4- $\text{C}_{10}\text{H}_6(\text{COCl})_2$  and  $s\text{-C}_6\text{H}_3\text{Me}_3$  give (by A) (VIII) (45%) and some (probably) mesityl 4-cyano-1-naphthyl ketone, m.p.  $134^\circ$  (corr.) (arising from the intermediate 4:1- $\text{CN}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ ). R. S. C.

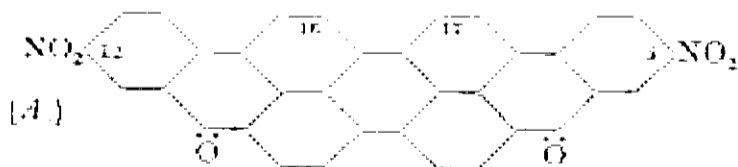
**Addition of magnesium methyl iodide to mesityl tert.-butyl diketone.** R. C. Fuson and J. A. Robertson [and, in part, J. W. Corse] (*J. Org. Chem.*, 1942, 7, 466—471; cf. A., 1939, II, 508).—Each of the CO groups of mesityl  $\text{Bu}^t$  diketone (I) reacts with  $\text{MgMeI}$  in the  $\alpha\beta$ -manner forming the corresponding ketol. If the condensation of  $\text{Bu}^t\text{CO}\cdot\text{CHO}$  with  $s\text{-C}_6\text{H}_3\text{Me}_3$  in presence of  $\text{AlCl}_3$  is carried out at a low temp. over a long period of time the main product is mesityltert.-butylcarbinol (II), m.p.  $44^\circ$ , instead of pivalylmesitylcarbinol (III), m.p.  $117\text{--}118^\circ$ . (II) affords an acetate, m.p.  $68^\circ$ , and is converted by  $\text{NaOEt--EtOH}$  at  $75^\circ$  under  $\text{N}_2$  into (III), which itself is unchanged under these conditions. (II) or (III) is oxidised

by  $\text{CuSO}_4$  in aq.  $\text{C}_6\text{H}_5\text{N}$  at  $100^\circ$  to (I), b.p.  $115\text{--}118^\circ/2\text{ mm.}$  (oxime, m.p.  $139^\circ$ ), in 83% yield. (I) is hydrogenated ( $\text{PtO}_2$  in  $\text{EtOH}$ ) to (III). (II) is reduced ( $\text{Cu chromite-EtOH-H}_2$  at  $175^\circ/1500\text{ lb.}$ ) to  $\alpha$ -mesityl- $\beta$ -tert.-butylethylene glycol, m.p.  $84\text{--}85^\circ$  (diacetate, m.p.  $73\text{--}74^\circ$ ), which is dehydrated by boiling, dil.  $\text{H}_2\text{SO}_4$  to 2:4:6-trimethylbenzyl  $\text{Bu}^\gamma$  ketone, m.p.  $80\text{--}81^\circ$  (oxime, m.p.  $147^\circ$ ), which does not contain active H. (I) and  $\text{MgMeI}$  in  $\text{Et}_2\text{O}$  afford mesitylmethyl-tert.-butylcarbinol (IV), m.p.  $81\text{--}82^\circ$  (acetate, m.p.  $77^\circ$ ), which contains 1 active H (Zerevitinov), and pivalylmesitylmethylcarbinol (V), m.p.  $104\text{--}105^\circ$ , which contains 1 active H but also does not give an acetate.  $\text{AcOH-60\% H}_2\text{SO}_4$  at  $100^\circ$  converts (IV) into  $\text{COMeBu}^\gamma$  and  $s\text{-C}_6\text{H}_3\text{Me}_3$  whilst 50%  $\text{H}_2\text{SO}_4$  at  $100^\circ$  transforms (V) into  $\alpha$ -mesitylvinylyl  $\text{Bu}^\gamma$  ketone (VI), b.p.  $112^\circ/3\text{ mm.}$ , reduced ( $\text{PtO}_2$  in  $\text{EtOH}$ ) to  $\alpha$ -mesitylethyl  $\text{Bu}^\gamma$  ketone (VII), m.p.  $86^\circ$ , which does not react with  $\text{Ac}_2\text{O-C}_6\text{H}_5\text{N}$ . Similar reduction of (VI) followed immediately by aeration of the solution gives the enol peroxide,  $\text{CMe(C}_6\text{H}_3\text{Me}_3)_2\text{O}$ , m.p.  $106^\circ$ . Mesityl  $\text{Bu}^\gamma$  ketone does not appear to react with  $\text{MgMeI}$  in boiling  $\text{Bu}^\alpha_2\text{O}$ . H. W.

**Mechanism for the formation of anthraquinone from  $\alpha$ -benzoylbenzoic acid.** M. S. Newman (*J. Amer. Chem. Soc.*, 1942, **64**, 2324—2325).—Addition of  $\alpha\text{-C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$  (I) in 98—99%  $\text{H}_2\text{SO}_4$  to cold  $\text{MeOH}$  gives 60% of a 40:56 mixture of  $\psi$ - and normal esters with 30% of unchanged (I). The  $\psi$ -ester is the primary product, being shown to be partly isomerised under the experimental conditions. Formation of anthraquinone (II) from (I) proceeds by the reactions:  $(\text{I}) + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{HSO}_4^\cdot + \text{H}_3\text{O}^+ + \alpha\text{-C}_6\text{H}_4\text{C}(\text{CO})^\cdot\text{O} \rightarrow \alpha\text{-C}_6\text{H}_4\text{Bz}\cdot\text{C}^\cdot\text{O} \rightarrow (\text{II}) + \text{H}^\cdot$ . R. S. C.

**Structure of 2-nitroindane-1:3-dione.** G. Wanag and J. Bungs (*Ber.*, 1942, **75**, [B], 987—990).—Comparative titrations of 2-nitroindane-1:3-dione (I) and Et indane-1:3-dione-2-carboxylate (II) in  $\text{C}_6\text{H}_6$ ,  $\text{Et}_2\text{O}$ ,  $\text{AcOH}$ ,  $\text{EtOH}$ , and  $\text{H}_2\text{O}$  with Br in the same solvents show that (I) is strongly isomerised in  $\text{H}_2\text{O}$  and  $\text{EtOH}$  but much less markedly in  $\text{Et}_2\text{O}$  and  $\text{C}_6\text{H}_6$  whereas (II) is more uniformly isomerised (66—90%) in different solvents. Isomerisation of (II) occurs very rapidly in  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ , and  $\text{AcOH}$  but slowly in  $\text{Et}_2\text{O}$  and  $\text{C}_6\text{H}_6$ . In any given solvent the behaviour of (I) differs from that of (II) and hence from that of a true keto-enol. Hence (I) isomerises to the ketonitronic acid,  $\text{C}_6\text{H}_4\text{C}(\text{CO})^\cdot\text{C}^\cdot\text{N}(\text{O})\cdot\text{OH}$ . H. W.

**Dinitrodibenzanthrone.** D. J. Bennett, R. R. Pritchard, and J. L. Simonsen (*J.C.S.*, 1943, 31—33).—The dinitrodibenzanthrone ( $\text{Bz-2-Bz-2'-dinitroviolanthrone}$ ) (I) (prep. described) of Maki *et al.* (A., 1936, 338) cannot be the 16:17-derivative since oxidation with aq.  $\text{CrO}_3\text{-H}_2\text{SO}_4$  gives a dinitro-2:2'-dianthraquinonyl-1:1'-dicarboxylic acid (II), amorphous, m.p.  $>400^\circ$  ( $\text{Me}_2$ , blackens at  $218^\circ$ ,



gradual decomp.  $>218^\circ$ , and  $\text{Et}_2$  ester, sinters at  $169\text{--}173^\circ$ , m.p.  $179\text{--}189^\circ$ , decomp.  $>190^\circ$ ). (I) may be (A). (II) and aq.  $\text{Fe}(\text{OH})_2\text{-NaOH}$  give the  $(\text{NH}_2)_2$ -acid; the tetrazonium sulphate and Zn dust in boiling  $\text{C}_6\text{H}_{11}\cdot\text{OH}$  afford 2:2'-dianthraquinonyl-1:1'-dicarboxylic acid ( $\text{Me}_2$  ester, decomp.  $\sim 374^\circ$ ), also obtained by oxidising dibenzanthrone (III). The magnetic susceptibilities of (III) and 3:3'-dibenzanthronyl are  $-0.32 \times 10^{-6}$  and  $-0.54 \times 10^{-6}$ , respectively. A. T. P.

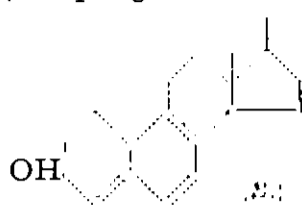
**Substituted anthraquinones.**—See B., 1943, II, 75.

#### IV.—STEROLS AND STERIOD SAPOGENINS.

**Catalytic reduction of cholesterol  $\alpha$ -oxide.** H. E. Stavely (*J. Amer. Chem. Soc.*, 1942, **64**, 2723—2724).—Cholesterol  $\alpha$ -oxide (I) and  $\text{H}_2\text{-Pd-AcOH}$  give slowly a mixture, which after acetylation ( $\text{Ac}_2\text{O-C}_6\text{H}_5\text{N}$ ) and chromatography gives cholestanyl acetate, cholestane-3:5-diol monoacetate, m.p.  $181^\circ$  (lit.  $177^\circ$ ) [free diol, m.p.  $216\text{--}217^\circ$  (lit.  $201^\circ$ )], and  $\alpha$ -cholestane-3:5:6-triol diacetate [also obtained from the acetate of (I) and hot  $\text{AcOH}$ ]. R. S. C.

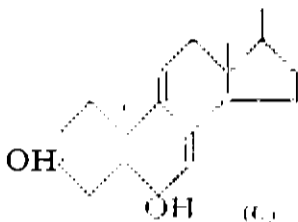
(A) Action of mercuric acetate on  $\Delta^6:8$ -cholestadien-3-ol (*isodehydrocholesterol*). A. Windaus, U. Riemann, and G. Zühlsdorff. (B) Action of lead tetra-acetate on *isodehydrocholesterol*. A. Windaus, U. Riemann, H. H. Rüggeberg, and G. Zühlsdorff (*Annalen*, 1942, **552**, 135—142, 142—152; cf. A., 1938, II, 185).—(A) *isodehydrocholesteryl p*-nitrobenzoate (I) in  $\text{CHCl}_3$  and  $\text{Hg}(\text{OAc})_2$  in  $\text{AcOH}$  rapidly yield  $\text{HgOAc}$  and the *p*-nitrobenzoate (A), m.p.  $210\text{--}211^\circ$ ,  $[\alpha]_D^{20} - 116.2^\circ$  in  $\text{CHCl}_3$ , of an unidentified alcohol,  $\text{C}_{27}\text{H}_{44}\text{O}_2$ , which does not react with  $\text{NH}_2\text{OH}$ , is probably dihydric, contains 4 double linkings, and arises from *isodehydrocholesterol* (II) by reaction with 3 O. *isodehydrocholesteryl 3:5-dinitrobenzoate* yields a similar ester,  $\text{C}_{34}\text{H}_{42}\text{O}_7\text{N}_2$ , m.p.  $223\text{--}224^\circ$ . After removal of (A) an amorphous material remains which is hydrolysed to a doubly unsatur-

ated, dihydric alcohol (III),  $\text{C}_{27}\text{H}_{44}\text{O}_2$ , m.p.  $228^\circ$ ,  $[\alpha]_D^{20} - 51.4^\circ$  in  $\text{C}_6\text{H}_5\text{N}$  (*di-3:5-dinitrobenzoate*, m.p.  $172^\circ$ ). It is converted by boiling  $\text{Ac}_2\text{O}$  into a *cholestatrienyl acetate* (IV), m.p.  $102\text{--}103^\circ$  (absorption max. at  $285\text{ m}\mu$ ), hydrolysed to an alcohol, m.p.  $99\text{--}100^\circ$ , which becomes yellow on exposure to air and is hydrogenated (Pt sponge in  $\text{EtOAc}$ ) to  $\alpha$ -cholesteryl acetate, m.p.  $76\text{--}77^\circ$ . The



mother-liquors from (III) yield a very characteristic 3:5-dinitrobenzoate,  $\text{C}_{34}\text{H}_{42}\text{O}_6\text{N}_2$ , m.p.  $219^\circ$ ,  $[\alpha]_D^{20} - 146^\circ$  in  $\text{CHCl}_3$ , hydrolysed to a monohydric alcohol (B), m.p.  $115^\circ$ , softens at  $108^\circ$ ,  $[\alpha]_D^{20} - 311^\circ$  in  $\text{CHCl}_3$ , shown by its absorption spectrum to have 4 double linkings in unbroken conjugation. It is formed from (I) by absorption of 2 O. It and its acetate, m.p.  $114\text{--}119^\circ$ ,  $[\alpha]_D^{19} - 225.5^\circ$  in  $\text{CHCl}_3$ , are very sensitive to air.

(B) (I) in  $\text{CHCl}_3$  is converted by  $\text{Pb}(\text{OAc})_4$  in  $\text{AcOH}$  at  $0^\circ$  and subsequently at room temp. into a *cholestatrienyl p*-nitrobenzoate (V), m.p.  $167\text{--}168^\circ$  (turbid), hydrolysed by alkali to a cholestatrienol, m.p.  $\sim 100^\circ$ ,  $[\alpha]_D^{20} - 81.2^\circ$  in  $\text{CHCl}_3$ , [acetate (VI), m.p.  $103\text{--}104^\circ$ ,  $[\alpha]_D^{20} - 77.6^\circ$  in  $\text{CHCl}_3$ ; 3:5-dinitrobenzoate, m.p.  $198^\circ$ ,  $[\alpha]_D^{20} - 65.0^\circ$  in  $\text{CHCl}_3$ ], which becomes yellow in air. The mother-liquors from (V) yield an amorphous residue hydrolysed to a mixture of cholestadienediols the composition of which varies greatly with slight differences in experimental technique. The ethereal solution deposits (III), better obtained by use of  $\text{Hg}(\text{OAc})_2$ . The more freely sol. material is purified through its additive products with digitonin and then yields a *di-3:5-dinitrobenzoate*, m.p.  $176^\circ$ , hydrolysed to a *cholestadienediol*, m.p.  $196^\circ$ , which may not be quite homogeneous. It and the non-cryst. residues obtained from it are transformed by boiling  $\text{Ac}_2\text{O}$  into a mixture of cholestatrienyl acetates similar to (IV). The chief portion has  $[\alpha]_D^{20} - 77^\circ$  but contains 10—20% of a strongly dextrorotatory isomeride the parent alcohol of which appears identical with  $\Delta^5:7:9(11)$ -cholestatrienol derived from 7-dehydrocholesterol or isopyrovitamin- $\text{D}_3$  by oxidation with  $\text{Hg}(\text{OAc})_2$ . The constitution (C) is ascribed to (III). Re-examination of the action of  $\text{BzO}_2\text{H}$  on (II) shows that the acetate, m.p.  $148^\circ$ , of cholestatrienol can be directly isolated by crystallisation from  $\text{COMe}_2\text{-MeOH}$ ; the mother-liquors therefrom contain (VI). H. W.



**Isolation of androsterone sulphate.** E. H. Venning, M. M. Hoffman, and J. S. L. Browne (*J. Biol. Chem.*, 1943, **146**, 369—379).—A cryst. conjugated androgen *Na androsterone sulphate* (I),  $\text{C}_{19}\text{H}_{28}\text{O}_2\cdot\text{SO}_3\text{Na}$ , m.p.  $144^\circ$  or  $+ \text{H}_2\text{O}$ , m.p.  $\sim 190^\circ$  (decomp.) (semicarbazone, m.p.  $245^\circ$ ), is isolated (details given, including a final chromatographic separation) from the urine of a man with an interstitial cell tumour of the testis. Acid hydrolysis of (I) affords (chromatographic analysis) variable amounts of androsten-17-one and androsterone. Synthetic dehydroisoandrosterone sulphate is hydrolysed by  $\text{HCl}$  to dehydroisoandrosterone and 3-chloro- $\Delta^5$ -androsten-17-one. A. T. P.

**Steroids and sex hormones. LXXXVIII. Oxidation of  $\Delta^4:17$ -pregnadien-3-one by monoperphthalic acid.** L. Ruzicka, M. W. Goldberg, and E. Hardegger (*Helv. Chim. Acta*, 1942, **50**, 1297—1305).— $\Delta^4:17$ -Pregnadien-3-one (I) [semicarbazone, m.p.  $224\text{--}226^\circ$  (decomp.)] is converted by  $\text{OsO}_4$  followed by  $\text{Na}_2\text{SO}_3$  into  $\Delta^4:17:20$ -dihydroxypregnen-3-one, m.p.  $204\text{--}205^\circ$ , oxidised by  $\text{Pb}(\text{OAc})_4$  in  $\text{AcOH}$  at room temp. to  $\Delta^4$ -androstene-3:17-dione, m.p.  $169\text{--}170^\circ$ . (I) is oxidised by  $\alpha\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  at room temp. to a mixture of isomerides,  $\text{C}_{21}\text{H}_{30}\text{O}_2$ , A, m.p.  $174.5\text{--}175.5^\circ$ ,  $[\alpha]_D^{20} + 82^\circ$  in  $\text{CHCl}_3$  [semicarbazone, m.p.  $227\text{--}228^\circ$  (decomp.)]; no colour with  $\text{C}(\text{NO}_2)_4$ , B (main product), m.p.  $188.5\text{--}190^\circ$ ,  $[\alpha]_D^{20} + 106^\circ$  in  $\text{CHCl}_3$  [semicarbazone, m.p.  $217\text{--}218^\circ$  (decomp.)]; no colour with  $\text{C}(\text{NO}_2)_4$ , and C, m.p.  $189\text{--}190^\circ$ ,  $[\alpha]_D^{20} + 111^\circ$  in  $\text{CHCl}_3$  [semicarbazone, decomp.  $200^\circ$ , m.p.  $207^\circ$ ; yellow colour with  $\text{C}(\text{NO}_2)_4$ ]. C gives an acetate, m.p.  $152.5\text{--}153.5^\circ$ , with  $\text{Ac}_2\text{O-C}_6\text{H}_5\text{N}$ , which do not affect A or B. The absorption spectra of A, B, and C are almost identical and characteristic of  $\alpha\beta$ -unsaturated ketones. A and B are possibly oxido-compounds and C a doubly unsaturated, CO-alcohol. M.p. are corr. (vac.). H. W.

**5-Methyl-2-ethylpyridine, a dehydrogenation product of solanidine.**—See A., 1943, II, 103.

#### V.—TERPENES AND TRITERPENOID SAPOGENINS.

**Essential oil of *Cupressus macrocarpa*.**—See B., 1943, III, 62.

**Vetiverone.** S. Sabetay and L. Trabaud (*Helv. Chim. Acta*, 1942, **25**, 1187).—A claim for priority against Naves (A., 1942, II, 371). H. W.

**Isolation of lupeol from the osage orange (*Maclura pomifera*, Raf.).** L. J. Swift and E. D. Walter (*J. Amer. Chem. Soc.*, 1942, **64**, 2539—2540).—Dry osage oranges (1 kg.) yield to light petroleum a mixture, whence chromatography (Al silicate) and alkaline hydrolysis afford lupeol (I) (2.3 g.), for which crystallo-optical properties and a

photomicrograph are given. With conc.  $\text{H}_2\text{SO}_4\text{-Ac}_2\text{O-CHCl}_3$ , (I) gives a red colour, also given by the dried latex of the fruit.

R. S. C.

**Phenolic behaviour of buchu-camphor and its derivatives. II. Comparison with phenols and keto-enols [in pH of dilute aqueous solutions].** (Signa.) C. Straneo (*Gazzetta*, 1941, 71, 646—647; cf. A., 1940, II, 136).—The pH (quinhydrone electrode) of 0.001N-aq. buchu-camphor (I), 6.65, is comparable with that of diphenols; in the OMe ether of (I) and in its 1- and 8- (alcoholic) -OH-derivatives the pH in 0.01N- and 0.001N-aq. solutions is comparable with that of monophenols (II). The pH of methylcyclohexane-1:2-diones (III) is slightly > that of (II), suggesting that in (III) both CO groups can enolise.

E. W. W.

**Sesquiterpenes. LV. Stepwise degradation of norcedrenedicarboxylic acid.** P. A. Plattner, G. W. Kusserow, and H. Klaut (*Helv. Chim. Acta*, 1942, 25, 1345—1364).—In the prep. of norcedrenedicarboxylic acid (I) according to Ruzicka *et al.* (A., 1929, 932), dihydroxycedranone, (?)  $\text{C}_{15}\text{H}_{24}\text{O}_3$ , m.p. 126—127° (semicarbazone, m.p. 181—182°; p-nitrobenzoate, m.p. 175°), is obtained as by-product; it does not give a yellow colour with  $\text{C}(\text{NO}_2)_4$  or react with  $\text{FeCl}_3$ . (I), has m.p. 209°,  $[\alpha]_D^{25} -39.4^\circ$  in  $\text{CHCl}_3$ , and is best obtained (with  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  and neutral compounds) by the oxidation of cedrenol in  $\text{COMe}_2$  by  $\text{KMnO}_4$  and of the acidic product by  $\text{HNO}_3$  (d 1.4). (I) is transformed by  $\text{H}_2\text{SO}_4\text{-MeOH}$  into the Me H ester, m.p. 98.5—99.5°, and by  $\text{CH}_2\text{N}_2$  into the Me<sub>2</sub> ester (II),  $[\alpha]_D^{25} -43.5^\circ$  in MeOH, partly hydrolysed by alkali to the Me H ester, m.p. 130—131°. Isomerisation is not observed when (I) or cedrenedicarboxylic acid is heated with conc. HCl at 180°, when the anhydride of (I) is heated at 210—220°, or when (II) is boiled with NaOMe-MeOH. The monocarboxylic acid,  $\text{C}_{12}\text{H}_{18}\text{O}_2$ , m.p. 90—90.5°, obtained by bromination of (I) followed by decarboxylation and removal of HBr does not show the absorption typical of  $\alpha\beta$ -unsaturation. Its Me ester is oxidised by  $\text{BzO}_2\text{H}$  in  $\text{CHCl}_3$  to the oxido-ester,  $\text{C}_{13}\text{H}_{20}\text{O}_3$ , b.p. 132—133°/12 mm.,  $[\alpha]_D -42.3^\circ$  in MeOH, transformed by boiling aq. dioxan into the (OH)<sub>2</sub>-ester,  $\text{C}_{13}\text{H}_{22}\text{O}_4$ , m.p. 105°,  $[\alpha]_D -36^\circ$  in MeOH, with smaller amounts of two isomerides, m.p. 134°,  $[\alpha]_D -63^\circ$  in MeOH, and m.p. 120—120.5°,  $[\alpha]_D -8^\circ$  in MeOH, respectively. With an excess of Br followed by  $\text{CH}_2\text{N}_2$ , (I) yields Me<sub>2</sub> bromonorcedrenedicarboxylate (III), m.p. 61—62°,  $[\alpha]_D -26.8^\circ$  in MeOH, with some Me H ester, m.p. 195—196°. (III) retains Br somewhat firmly but when treated with KOH in boiling aq. dioxan, followed by  $\text{CH}_2\text{N}_2$ , fractional distillation, and eventual hydrolysis, gives the monocarboxylic acid,  $\text{C}_{12}\text{H}_{18}\text{O}_2$ , m.p. 90—91° (loc. cit.), Me<sub>2</sub> dihydronorcedrenedicarboxylate (IV),  $[\alpha]_D^{25} -70^\circ$  in  $\text{CHCl}_3$ , and Me<sub>2</sub> hydroxynorcedrenedicarboxylate, m.p. 105°. With KOAc in  $\text{COMe}_2$  at 150° (or 180° with large charges) (III) gives (IV), hydrolysed with difficulty to the acid (V), m.p. 212—213°,  $[\alpha]_D -91^\circ$  or  $-87^\circ$  ( $c = 2.7$  or 1.2) in MeOH, hydrogenated to (I) and apparently transformed by boiling  $\text{Ac}_2\text{O}$  into a polymeric anhydride. (V) is oxidised by  $\text{KMnO}_4$  in alkaline solution to the ketodicarboxylic acid,  $\text{C}_{12}\text{H}_{18}\text{O}_5\cdot\text{H}_2\text{O}$  (also anhyd.), m.p. 142.5—143°,  $[\alpha]_D -35^\circ$  in MeOH [p-nitrophenylhydrazone,  $\text{C}_{18}\text{H}_{23}\text{O}_6\text{N}_3$ , m.p. 182—183°; Me<sub>2</sub> ester, b.p.  $\sim 110^\circ/1$  mm.,  $[\alpha]_D +21^\circ$  in MeOH (p-nitrophenylhydrazone, m.p. 106°)]. This is oxidised [ $\text{Pb}(\text{OAc})_4$  in AcOH at room temp. and then at 70—80°] to the anhydride (VI),  $\text{C}_{11}\text{H}_{16}\text{O}_3$ , b.p. 125°/high vac.,  $[\alpha]_D^{25} -22.9^\circ$  in MeOH, hydrolysed to the dicarboxylic acid, m.p. 88.5—89°,  $[\alpha]_D^{25} +13^\circ$ ,  $+17.9^\circ$  ( $c = 0.6, 1.15$ ) in MeOH,  $[\alpha]_D^{25} -4.9^\circ$  in  $\text{CHCl}_3$  (Me<sub>2</sub> ester, b.p.  $\sim 80^\circ$ /high vac.,  $[\alpha]_D^{25} +26.3^\circ$  in MeOH). The acid is obtained in less pure form and poorer yield by oxidation with  $\text{H}_2\text{O}_2$ . Attempts to cyclise it by CaO at 260—320° give (VI). (VI) is converted by  $\text{PBr}_3$  followed by Br, esterification with MeOH, fractional distillation, and hydrolysis into the lactonecarboxylic acid,  $\text{C}_{11}\text{H}_{16}\text{O}_4$ , m.p. 187°. M.p. are corr.

H. W.

**Sesquiterpenes. LVI. Degradation of dihydroeudesmol by chromic acid.** L. Ruzicka, P. A. Plattner, and A. Fürst [and, in part, A. Ahl] (*Helv. Chim. Acta*, 1942, 25, 1364—1374).—Eudesmol is reduced (Raney Ni-EtOH- $\text{H}_2$  at 100°/100 atm.) to dihydroeudesmol (I), m.p. 86—87°,  $[\alpha]_D +16.8^\circ$  in  $\text{CHCl}_3$ , which is dehydrated with about equal readiness when it is treated with  $\text{KHSO}_4$  or when converted into the hydrochloride and then treated with KOH-EtOH. The products obtained by decomp. of the ozonide of the resulting dihydroeudesmene by  $\text{H}_2\text{O}$  give indefinite semicarbazones; reductive fission leads to more tractable products, but the yields are unsatisfactory. (I) is oxidised by  $\text{CrO}_3$  in AcOH at 75—80° to 3-keto-5:9-dimethyldecahydronaphthalene (II) (semicarbazone, m.p. 222°,  $[\alpha]_D +26^\circ$  in AcOH) and an acid, probably 1:3-dimethylcyclohexane-1:2-diacetic acid, m.p. 141—143° [Me<sub>2</sub> ester,  $[\alpha]_D +5.5^\circ$ ,  $+4.6^\circ$  ( $c = 1.61; 1.30$ ) in  $\text{COMe}_2$ ]. (II) is converted by PhCHO and KOH in aq. EtOH into the mono-, m.p. 141—143°,  $[\alpha]_D +20.63^\circ$  in EtOH, and by PhCHO and HCl in Et<sub>2</sub>O and treatment of the product with NaOAc in AcOH into the di-, m.p. 198—200°,  $[\alpha]_D^{17} -14.6^\circ$  in  $\text{CHCl}_3$ , -benzylidene derivative. Ozonisation of the last named compound leads to (?) 1:3-dimethylcyclohexane-2-carboxylic-1-acetic acid, m.p. 132—134°,  $[\alpha]_D +47.1^\circ$  in  $\text{COMe}_2$  (Me<sub>2</sub> ester,  $[\alpha]_D +45.3^\circ$  in  $\text{COMe}_2$ ; Me ester anilide, m.p. 100—102°,  $[\alpha]_D +78^\circ$  in  $\text{COMe}_2$ ). M.p. are corr.

H. W.

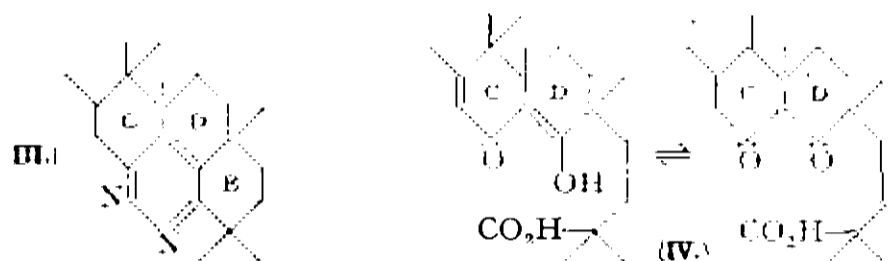
**Triterpenes. LXVIII.  $\alpha$ -Elemolic acid.** L. Ruzicka, E. Rey, and M. Spillmann (*Helv. Chim. Acta*, 1942, 25, 1375—1402).—Since identical CO-acids are not obtained from  $\alpha$ - (I) and  $\beta$ - (II) -elemolic acids, these triterpene acids cannot be epimerides with respect to the sec.-OH. (I) and (II) lose 3 C as  $\text{COMe}_2$  when ozonised or oxidised by  $\text{CrO}_3$  or  $\text{KMnO}_4$  with production of a new  $\text{CO}_2\text{H}$ ; hence the readily hydrogenated double linking in (I) and (II) must be present in a side-chain with terminal  $\cdot\text{CH}\cdot\text{CMe}_2$ . The difficultly reactive double linking of (I) is oxidised by  $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  to an oxido-compound whereas the latent, not yet hydrogenated double linking of (II) is not affected by the oxidant and in this respect resembles the double linking of  $\alpha$ -amyrin. A partial, mutual transformation in the two series is observed during many oxidations and hydrogenations which possibly depend on a displacement of the difficultly reactive double linking. Since the active double linking is in the same position in the two elemolic acids it is highly probable that they differ from one another solely in the position of the difficultly reactive linking and have an otherwise similar structure. Since the relationship between (I) and (II) is very similar to that between lanosterol and cryptosterol in respect of oxidation with  $\text{CrO}_3$ , ozonisation, hydrogenation, and dehydrogenation by Se it is probable that there is a close analogy between these groups of tetracyclic triterpene derivatives. (I), m.p. 224—225°,  $[\alpha]_D -24.0^\circ$ , isolated from Manila elemi resin (A., 1942, II, 266) is shown to be homogeneous by further treatment with Girard reagent T and by chromatography of its Me ester, m.p. 143—144°,  $[\alpha]_D -17.6^\circ$ , in light petroleum over  $\text{Al}_2\text{O}_3$ . The following new or revised data are recorded: acetyl- $\alpha$ -elemolic acid (III), m.p. 241—242°,  $[\alpha]_D -36.1^\circ$ ;  $\alpha$ -elemolic acid (IV), m.p. 286—287°,  $[\alpha]_D -76.0^\circ$  (Me ester, m.p. 161—162°,  $[\alpha]_D -90.2^\circ$ ; oxime, m.p. 227—228°,  $[\alpha]_D -84.4^\circ$ ); dihydro- $\alpha$ -elemolic acid, m.p. 309—310°,  $[\alpha]_D -97.0^\circ$  (oxime, m.p. 233—234°,  $[\alpha]_D -117.2^\circ$ ); dihydro- $\alpha$ -elemolic acid, m.p. 237—238°,  $[\alpha]_D -22.6^\circ$  [acetate (VI), m.p. 250—251°,  $[\alpha]_D -33.1^\circ$ ]; acetyl- $\alpha$ -elemolyl chloride, m.p. 209—210°,  $[\alpha]_D -120^\circ$ ;  $\beta$ -elemolic acid, m.p. 224—225°,  $[\alpha]_D +43.2^\circ$ . Catalytic hydrogenation ( $\text{PtO}_2$  in AcOH) of (I) gives (V) and (after methylation) Me acetyldihydro- $\alpha$ -elemolate (VII), m.p. 130.5—131°,  $[\alpha]_D -40.7^\circ$ , and Me dihydro- $\alpha$ -elemolate. (VI) is obtained by catalytic hydrogenation ( $\text{PtO}_2$  in AcOH) of (III); under similar conditions Me  $\alpha$ -elemolate is reduced to (VII). (III) in EtOH containing Raney Ni at 60° is hydrogenated to (VI), whereas (I) gives (V) when reduced in EtOH containing Raney Ni at 200°/160 atm. (I) is reduced ( $\text{H}_2$  at 180°/60 atm.,  $\text{PtO}_2\text{-AcOH}$ ) to a dihydrodeoxo- $\alpha$ -elemolic acid, m.p. 247—248°,  $[\alpha]_D +3.6^\circ$ . (IV) is transformed by  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  followed by  $\text{NaOEt-EtOH}$  at 190° into deoxy- $\alpha$ -elemolic acid, m.p. 263—263.5°,  $[\alpha]_D -20.8^\circ$ , hydrogenated ( $\text{PtO}_2$  in AcOH) to dihydrodeoxo- $\alpha$ -elemolic acid, m.p. 284—285°,  $[\alpha]_D -51.7^\circ$  (Me ester, m.p. 118.5—119.5°,  $[\alpha]_D -56.0^\circ$ ). Me  $\alpha$ -elemolate is converted by  $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  in  $\text{CHCl}_3$  into its dioxide, m.p. 203—204°,  $[\alpha]_D -6.0^\circ$ , which does not give a yellow colour with  $\text{C}(\text{NO}_2)_4$  and could not be satisfactorily hydrolysed in acid, alkaline, or neutral solution; large amounts of non-cryst. material are simultaneously formed. (VII) is oxidised by  $\text{SeO}_2$  in aq. dioxan at 230° to an isomeric Me acetyl- $\alpha$ -elemolate (VIII), m.p. 126—127°,  $[\alpha]_D -89.0^\circ$ , which could not be hydrogenated ( $\text{PtO}_2$  in AcOH); it is oxidised by  $\text{CrO}_3$  in AcOH at 100° to Me diketeoacetyldihydro- $\alpha$ -elemolate, m.p. 144.5—145.5°,  $[\alpha]_D -26.9^\circ$ , also obtained apparently by oxidising the known Me acetyldihydro- $\alpha$ -elemolate with  $\text{CrO}_3$ . (I) is oxidised by  $\text{CrO}_3$  in AcOH to (IV) and  $\beta$ -elemolic acid, m.p. 225°,  $[\alpha]_D +43.2^\circ$  (Me ester, m.p. 103—104°,  $[\alpha]_D +34.5^\circ$ ). (IV) is converted by Na and EtOH followed by  $\text{CH}_2\text{N}_2$  into Me epi- $\alpha$ -elemolate (IX), m.p. 141.5°,  $[\alpha]_D -49.2^\circ$ , which does not give a cryst. acetate and is hydrogenated ( $\text{PtO}_2$  in AcOH at room temp.) to Me epidihydro- $\alpha$ -elemolate, m.p.  $\sim 100^\circ$  and 151—152° after re-solidification at 130—140°,  $[\alpha]_D -50.3^\circ$ . (IX) is oxidised by  $\text{CrO}_3$  in AcOH to Me  $\alpha$ -elemolate, m.p. 161—162°,  $[\alpha]_D -89.0^\circ$ . (IV) is hydrogenated ( $\text{PtO}_2$  in AcOH at 100°) to the  $\text{H}_2$ -compound and epidihydro- $\alpha$ -elemolic acid, m.p. 265—265.5°,  $[\alpha]_D -60.0^\circ$ ; the latter substance is produced under the same conditions but at room temp.  $\text{CrO}_3$  and (VIII) in AcOH at 50° afford (after esterification) Me<sub>2</sub> trisnoracetyl- $\alpha$ -tritelemonoldicarboxylate, m.p. 133—135°. Ozonisation of Me  $\alpha$ -elemolate and decomp. of the ozonide by boiling  $\text{H}_2\text{O}$  gives Me<sub>2</sub> trisnor- $\alpha$ -tritelemonedicarboxylate, m.p. 161—161.5°,  $[\alpha]_D -146.0^\circ$ . Dehydrogenation of (I) by Se at 350° affords a hydrocarbon mixture which gives additive products,  $\text{C}_{22}\text{H}_{17}\text{O}_6\text{N}_3$ , m.p. 145—146°, and  $\text{C}_{22}\text{H}_{17}\text{O}_6\text{N}_3$  or  $\text{C}_{23}\text{H}_{19}\text{O}_6\text{N}_3$ , m.p. 159—160°, with  $\text{C}_6\text{H}_3(\text{NO}_2)_3$ , 1:7:8-trimethylphenanthrene, m.p. 146—147° [additive product, m.p. 192—192.5°, with  $\text{C}_6\text{H}_3(\text{NO}_2)_3$ , 1:7-dimethylphenanthrene [isolated as the additive compound, m.p. 159—160°, with  $\text{C}_6\text{H}_3(\text{NO}_2)_3$  and as the picrate, m.p. 130—131°], and a homologue,  $\text{C}_{24}\text{H}_{18}$ , of picene, m.p. 345—346°. M.p. are corr. (vac.).  $[\alpha]_D$  are determined in  $\text{CHCl}_3$ .

H. W.

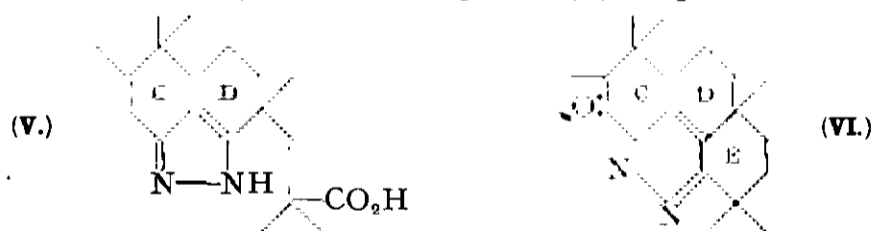
**Triterpenes. XLIX.  $\beta$ -Elemolic acid.** L. Ruzicka, H. Häusermann, and E. Rey (*Helv. Chim. Acta*, 1942, 25, 1403—1409).—Oxidation ( $\text{CrO}_3$  in AcOH) of acetyldihydro- $\beta$ -elemolic acid at room temp. gives diketeoacetyldihydro- $\beta$ -elemolic acid, m.p. 269—270°,  $[\alpha]_D +23.6^\circ$  in  $\text{CHCl}_3$  (Me ester, m.p. 176.5—177.5°,  $[\alpha]_D +35.6^\circ$  in  $\text{CHCl}_3$ ), which is shown by its absorption spectrum to contain

the group  $\text{CO}\cdot\text{C}\cdot\text{C}\cdot\text{CO}$ . It is hydrogenated ( $\text{PtO}_2$  in  $\text{AcOH}$ ) to (?) *ketoacetyl-tetrahydro- $\beta$ -elemolic acid*, m.p. 273—275°, which does not give a yellow colour with  $\text{C}(\text{NO}_2)_4$ . Treatment of  $\beta$ -elemonic acid (I) in  $\text{CCl}_4$  with  $\text{O}_3$  until the product fails to decolorise  $\text{Br}\cdot\text{H}_2\text{O}$  and decomp. of the product with hot  $\text{H}_2\text{O}$  yields  $\text{COMe}_2$  in considerable amount but a cryst. material could not be obtained from the acidic products. Similar treatment of  $\text{Me } \beta$ -elemonate (II) affords  $\text{COMe}_2$ , an acid (III),  $\text{C}_{28}\text{H}_{42}\text{O}_5$ , m.p. 210—211°,  $[\alpha]_D^{25} +37.5$  in  $\text{CHCl}_3$  (*Me* ester), which gives a marked yellow colour with  $\text{C}(\text{NO}_2)_4$ , and a non-cryst. neutral material, oxidised ( $\text{CrO}_3$  in  $\text{AcOH}$ ) to (III). (III) is also obtained by oxidation of (III) with  $\text{KMnO}_4$  in boiling  $\text{COMe}_2$  in addition to 80% of a neutral, amorphous substance. Hydrogenation ( $\text{PtO}_2$  in  $\text{EtOH}\cdot\text{AcOH}$  at room temp.) of deoxo- $\beta$ -elemonic acid affords *dihydrodeoxo- $\beta$ -elemonic acid* m.p. 259—260°,  $[\alpha]_D^{25} +9.35$  in  $\text{CHCl}_3$  (*Me* ester, m.p. 100—100.5°,  $[\alpha]_D^{25} +4.8$  in  $\text{CHCl}_3$ ), which gives a distinct yellow colour with  $\text{C}(\text{NO}_2)_4$ . (I) and anhyd.  $\text{HCO}_2\text{H}$  in  $\text{CHCl}_3$  at room temp. yield the substance,  $\text{C}_{31}\text{H}_{48}\text{O}_5$ , m.p. 240—242°; at higher temp. a cryst. material does not result. M.p. are corr. H. W.

**Triterpenes. LXX. Further transformations of  $\beta$ -amyradienedionol.** L. Ruzicka and O. Jeger (*Helv. Chim. Acta*, 1942, 25, 1409—1419).— $\beta$ -Amyradienedionol acetate is oxidised by  $\text{CrO}_3$  (cf. Simpson, A., 1938, II, 448) to its oxide (I), m.p. 290—291°, and a compound,  $\text{C}_{32}\text{H}_{42}(\text{O})_6$ , m.p. 288—290° (decomp.). (I) is hydrolysed by boiling  $\text{KOH}\cdot\text{MeOH}$  or by 10%  $\text{HCl}\cdot\text{MeOH}$  at  $\sim 200^\circ$  to  $\beta$ -amyradienedionol oxide (II), m.p. 310—312° (vac.; decomp.). (I) and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in  $\text{EtOH}$  at  $200^\circ$  give the pyridazine derivative (III), m.p. 292—293° (*Ac* derivative, m.p. 261°). (I) is converted by  $\text{KOH}\cdot\text{MeOH}$  at  $130^\circ$  into (II), at  $200^\circ$  into (II) and an acid (IV),



and at  $210^\circ$  into (IV) and an unidentified, non-cryst. product. (IV), m.p. 239—240° (*Me* ester, m.p. 114—115°; *acetate*, m.p. 157—158°), gives a dark yellow colour with  $\text{C}(\text{NO}_2)_4$ , a grey-green to black-green colour with  $\text{FeCl}_3$ , and is not lactonised at  $230^\circ/\text{vac}$ . It does not react with  $\text{NH}_2\text{OH}$  in  $\text{EtOH}$  at  $80\text{--}200^\circ$  but with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  at  $200^\circ$  yields the compound (V), m.p. 264—265°, also



obtained from (I),  $\text{KOH}$ , and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in  $\text{MeOH}$  at  $200^\circ$ . (III) is oxidised by  $\text{H}_2\text{O}_2$  in  $\text{AcOH}$  to a non-cryst. product acetylated to (VI), m.p. 253° (decomp.), which is reduced (Wolff-Kishner) to (III). M.p. are corr. H. W.

**Saponin of fenugreek seeds.** G. Soliman and Z. Mustafa (*Nature*, 1943, 151, 195—196).—The pure saponin (separation described), m.p. 190—200°, afforded in hydrolysis a cryst. mixture, m.p. 184°, of sapogenins from which a compound,  $\text{C}_{27}\text{H}_{42}\text{O}_3$ , m.p. 198° (free  $\text{OH}$ ; 2 inactive  $\text{O}$ ), was isolated. It appears to belong to the sarsasapogenin group. A. A. E.

**Saponins and sapogenins. XX. Bethogenin and trilloegenin, new sapogenins from *Trillium erectum*.** S. Lieberman, F. C. Chang, M. R. Barusch, and C. R. Noller (*J. Amer. Chem. Soc.*, 1942, 64, 2581—2583).—Hydrolysis of the extract of the root of *T. erectum* yields diosgenin, trillin (anhyd.), m.p. 269.5—271° (preheated bath),  $[\alpha]_D^{20} -103.4$ ,  $[\alpha]_{\text{Hg}}^{26} -127.2$  in dioxan (*acetate*, m.p. 204—205°,  $[\alpha]_D^{20} -71.4$ ,  $[\alpha]_{\text{Hg}}^{30} -80.2$  in dioxan), chlorogenin, bethogenin (I),  $\text{C}_{27}\text{H}_{40}\text{O}_4$ , m.p. 193—194°,  $[\alpha]_D^{24} -98.4$  in dioxan, and trilloegenin (II),  $\text{C}_{27}\text{H}_{48}\text{O}_4$ , m.p. 206—210°,  $[\alpha]_D^{24} -41.6$ ,  $[\alpha]_{\text{Hg}}^{24} -54.3$  in dioxan. (I) is unstable when kept or recrystallised, is unsaturated  $[\text{C}(\text{NO}_2)_4]$ , gives an *acetate*, m.p. 230—232°,  $[\alpha]_D^{24} -94.4$  in dioxan, and *benzoate*, m.p. 212—215°,  $[\alpha]_D^{24} -65.1$  in dioxan, shows 1 active  $\text{H}$ , with  $\text{H}_2\text{--PdO}\cdot\text{EtOAc}$  at 30 lb. and then  $\text{Ac}_2\text{O}\cdot\text{C}_6\text{H}_5\text{N}$  gives *tetrahydro-bethogenin diacetate*, m.p. 141—144°,  $[\alpha]_D^{24} -156$  in dioxan, and gives an *oxime*, m.p. 241—243°, but with  $\text{Ac}_2\text{O}$  does not isomerise. The side-chain of (II) may be open, since a *tetra-acetate*, m.p. 102—103°,  $[\alpha]_D^{24} 0$ ,  $[\alpha]_{\text{Hg}}^{24} -3.5$  in dioxan, is obtained by  $\text{Ac}_2\text{O}\cdot\text{NaOAc}$ . R. S. C.

## VI.—HETEROCYCLIC.

**Reaction of furoic acid with tetrahydronaphthalene.**—See A., 1943, II, 91.

**Preparation of  $\beta$ -2-furylacrylic acid.** S. Rajagopalan (*Proc. Indian Acad. Sci.*, 1942, A, 16, 163—166).— $\beta$ -2-Furylacrylic acid,

m.p.  $141^\circ$ , is obtained in 66—67% yield by heating an equimol. mixture of furfuraldehyde,  $\text{CH}_2(\text{CO}_2\text{H})_2$ , and  $\text{C}_5\text{H}_5\text{N}$  at  $100^\circ$  for 2 hr. H. W.

**Condensation of succinic acid with acetylacetone.** Z. F. Stefanovskaja, V. V. Dorofeev, and I. A. Trefiliev (*J. Gen. Chem. Russ.*, 1941, 11, 518—522).— $(\text{CH}_2\cdot\text{CO}_2\text{Na})_2$  and  $\text{CH}_2\text{Ac}_2$  in  $\text{Ac}_2\text{O}$  are heated for 20 hr. at  $100^\circ$ , and the product is treated with dil.  $\text{HCl}$  and extracted with  $\text{Et}_2\text{O}$ . The  $\text{Et}_2\text{O}$ -sol. fraction consists chiefly of a resinous acid, and this, heated with  $\text{H}_2\text{O}$  at  $100^\circ$  (12 hr.), yields 1-acetonyl-4-methylfuran-2-carboxylic acid, m.p. 121—122°. R. T.

**Halogen compounds derived from 2:5-diphenyl-3-methylfuran.** R. E. Lutz and C. E. McGinn (*J. Amer. Chem. Soc.*, 1942, 64, 2583—2585).—2:5-Diphenyl-3-methylfuran in  $\text{CHCl}_3$  gives, successively, the 4-Br-derivative (I), 4-bromo-2:5-di-p-bromophenyl-3-methyl- (II), m.p. 168—169°, and -3-bromomethyl-furan (III) (75%), m.p. 212—213°. Structures are proved by indifference of the products to  $\text{Zn}$  dust- $\text{AcOH}$ , except that (III) gives (II). With  $\text{HNO}_3\cdot\text{AcOH}$ , (I) gives *cis*- $\text{COPh}\cdot\text{CMe}\cdot\text{CBr}\cdot\text{COPh}$ , reduced by  $\text{Zn}$  dust- $\text{AcOH}$  to  $\text{COPh}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{COPh}$ . (II) and (III) give similarly *cis*- $\beta$ -bromo- $\alpha$ -di-p-bromophenyl- $\gamma$ -methyl- (IV) (91%), m.p. 119.5—120°, and - $\gamma$ -bromomethyl- $\Delta^2$ -butene- $\alpha$ -dione (V) (90%), m.p. 117—117.5°, both reduced by  $\text{SnCl}_2\cdot\text{AcOH}\cdot\text{conc. HCl}$  to 2:5-di-p-bromophenyl-3-methylfuran (VI), m.p. 158—159°. (VI) and *cis*- $\alpha$ -di-p-bromophenyl- $\beta$ -methyl- $\Delta^2$ -butene- $\alpha$ -dione (VII), m.p. 115—116° (unaffected by 1- $\text{CHCl}_3$ -light), are interconvertible by  $\text{HNO}_3$  and  $\text{SnCl}_2$ .  $\text{Zn}$  dust- $\text{AcOH}$  reduces (IV), (V), and (VII) to  $\alpha$ -di-p-bromophenyl- $\beta$ -methyl-butane- $\alpha$ -dione, m.p. 120—120.5°. R. S. C.

**Conversion of unsaturated 1:4-diketones into furans and hydroxyfuranones.** R. E. Lutz and C. E. McGinn (*J. Amer. Chem. Soc.*, 1942, 64, 2585—2588).—Further examples are provided of the greater ease of dehydration of *cis*- compared with *trans*- $\text{COPh}\cdot\text{CR}\cdot\text{CR}'\cdot\text{COPh}$ . Spatial as well as energy relations may be the cause, in accord with formation of some hydroxyfuranones from *cis*-diketones. *trans*- (I) (modified prep.) and *cis*- $\text{COPh}\cdot\text{CH}\cdot\text{CMe}\cdot\text{COPh}$  (II) [prep. from 2:5-diphenyl-3-methylfuran (III) by  $\text{HNO}_3\cdot\text{AcOH}$  at  $10^\circ$ ; 81% yield] with  $\text{HBr}\cdot\text{AcOH}$  give 4-bromo-2:5-diphenyl-3-methylfuran (IV) [also obtained from (III) by  $\text{Br}\cdot\text{CHCl}_3$ ], with  $\text{Zn}$  dust in  $\text{AcOH}$  give  $\text{CHMeBz}\cdot\text{CH}_2\text{Bz}$  (V), and with  $\text{SnCl}_2\cdot\text{conc. HCl}\cdot\text{AcOH}$  give (III) (96%) [also obtained from (V)], but with  $\text{Ac}_2\text{O}\cdot\text{H}_2\text{SO}_4$  at room temp. (II) gives 4-acetoxy-2:5-diphenyl-3-methylfuran (VI) (50—68%), m.p. 94—95°, and with  $\text{Bz}_2\text{O}\cdot\text{H}_2\text{SO}_4$  gives an oily *Bz*-compound, whereas (I) does not react; with  $\text{ZnCl}_2\cdot\text{Ac}_2\text{O}\cdot\text{AcOH}$  *trans*- but not *cis*- (2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}$ ) $_2$  gives the saturated diketone. (VI) could not be converted into the 4-Cl-compound. With  $\text{Br}\cdot\text{CCl}_4$ , (VI) gives 2-bromo-2:5-diphenyl-4-methyl-2:3-dihydrofuran-3-one, m.p. 88—89° (with boiling  $\text{EtOH}$  gives the 2-OEt compound), *cis*- $\text{COPh}\cdot\text{CMe}\cdot\text{CBr}\cdot\text{COPh}$  [prep. from (IV) by conc.  $\text{HNO}_3\cdot\text{AcOH}$  at  $80^\circ$ ] with  $\text{H}_2\text{SO}_4$  (2 drops) in  $\text{AcOH}$  at  $0^\circ$  gives 2-acetoxy-, with  $\text{H}_2\text{SO}_4$  in  $\text{AcCl}$  at  $0^\circ$  gives 2-chloro-, and with  $\text{HCl}\cdot\text{MeOH}$  gives 2-methoxy-2:5-diphenyl-4-methyl-1:2-dihydrofuran-2-one. 3-Bromo-2:4:5-triphenylfuran (prep. from  $\text{COPh}\cdot\text{CPh}\cdot\text{CH}\cdot\text{COPh}$  by 30%  $\text{HBr}\cdot\text{AcOH}$  at room temp.) gives similarly 2-acetoxy-, 2-chloro-, and 2-methoxy-2:4:5-triphenyl-1:2-dihydrofuran-3-one. R. S. C.

**Constitution of the photodimerisates of the coumarins and furocoumarins.** F. von Wessely and I. Plaichinger (*Ber.*, 1942, 75, [B], 971—976).—Evidence is adduced in favour of the view that the photodimerides of coumarins and furocoumarins are *cyclobutane* derivatives.  $\alpha$ -Dicoumarin (Ström, A., 1904, i, 505) could not be hydrogenated in cold or hot  $\text{AcOH}$  containing  $\text{Pd}$ .  $\text{Me}_2$  dicoumarate  $\text{Me}_2$  ether, m.p. 133.5—135° (corr.), softens at  $130^\circ$ , obtained from it by  $\text{Me}_2\text{SO}_4$  and  $\text{NaOH}$ , is similarly resistant. Analogously diherniarin (II) could not be hydrogenated. On the other hand the compound  $\left[\begin{smallmatrix} \text{O} & \text{CO} \\ | & // \\ \text{C}_6\text{H}_4 & \text{CH} \end{smallmatrix} \right]_2$  obtained by Dyson (*J.C.S.*, 1887, 51, 68) by condensing  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  with  $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$  readily absorbs 2  $\text{H}_2$  in presence of  $\text{Pd}\cdot\text{C}$  or under the action of  $\text{Na}\cdot\text{Hg}$ . The product obtained by the action of  $\text{Br}$  on (I) is a substitution compound, the constitution of which has not been determined. H. W.

**Synthetic experiments in the benzopyrone series. VI. Action of aluminium chloride on angelicin, psoralen, and related compounds.** B. Krishnaswamy and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, A, 16, 151—156).—Angelicin is converted by  $\text{C}_6\text{H}_6$  and  $\text{AlCl}_3$  at room temp. into 8- $\alpha$ - $\beta$ -diphenylethylumbelliferone, m.p. 205—206°, which gives a blue fluorescence in dil. alkali and a bright violet fluorescence in conc.  $\text{H}_2\text{SO}_4$ . Similarly, psoralen affords 6- $\alpha$ - $\beta$ -diphenylethylumbelliferone, m.p. 259—260°, transformed by  $\text{MeI}$  and  $\text{K}_2\text{CO}_3$  in anhyd.  $\text{COMe}_2$  into the *Me* ether, m.p. 172—173°. The following observations show that the coumarin ring is not involved and that the furan ring is the active centre: (a) coumarin (I) and 6-nitrocoumarin are unaffected; (b) umbelliferone and 4-methylumbelliferone *Me* ether undergo simple demethylation; (c) coumarone is polymerised too readily to allow condensation with  $\text{C}_6\text{H}_6$ ; (d) coumarilic acid (II) undergoes smooth addition to 3-phenyldihydro-

*coumarilic acid*, m.p. 143—144°. Coumaric acid resembles (II) in this reaction and differs from (I). H. W.

**Useful colour reactions of anthoxanthins and related compounds.** S. Rangaswami and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **A**, 16, 129—134).—The scope of the following colour reactions has been investigated using a large no. of natural and synthetic flavones (I), flavonols (II), flavonones (III), and certain related compounds: (a) reduction with Mg and HCl-EtOH, (b) reduction with Na-Hg and EtOH, and (c) Wilson's  $H_3BO_3$  test using a mixture of  $H_3BO_3$  and citric acid in  $COMe_2$ . For the first two reactions the nature of the colour depends in general on the no. of OH and OMe groups in the mol. Qualitatively it is not easy to effect minor distinctions between (I), (II), and (III). Wilson's test is very sp. for 5-hydroxy- and 5-methoxy-flavones and (II) and *o*-hydroxy- and methoxy-chalkones. It is not given by (III) and simple aromatic ketones which do not satisfy the sp. conditions. A combination of the three reactions gives much useful information. H. W.

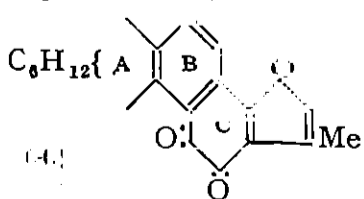
**Preparation of substances resembling tocopherol and flavonols from benzopyrylium salts.** P. Karrer and W. Fatzer (*Helv. Chim. Acta*, 1942, **25**, 1129—1138).—Passage of dry HCl into a solution of 2:5:4:6:1-(OH) $_2$ C $_6$ HMe $_2$ CHO and CPh $\cdot$ CH $_2$ OMe in anhyd. HCO $_2$ H at 0° and then at 20° leads to 6-hydroxy-3-methoxy-2-phenyl-5:7-dimethylbenzopyrylium chloride (I), hydrogenated (Pt in AcOH) to 6-hydroxy-2-phenyl-5:6-dimethylchroman-3-one, m.p. 141° (oxime, m.p. 216°), which does not contain OMe. (I) is transformed by NaOAc in MeOH into the *Me ether* (II), m.p. 179° (vac.) [analogously the *Et ether*, m.p. 163—164°, or 172° (vac.)], of the

Me CH:CBzOMe 6-hydroxy-3-methoxy-2-phenyl-5:7-dimethylbenzopyrylium base. (II) is oxidised by FeCl $_3$  to the *quinone* (III), m.p. 116°, which gives an absorption spectrum very similar to that of tocopherolquinone, and 6-hydroxy-2:3-dimethoxy-5:7-dimethylflavanone, m.p. 141° (*Me ether*, m.p. 117° after softening). H. W.

**Oxidation of benzopyrylium salts to flavonols.** P. Karrer and W. Fatzer (*Helv. Chim. Acta*, 1942, **25**, 1138—1140).—The double salt of FeCl $_3$  and 3-methoxy-2-phenylbenzopyrylium chloride passes in MeOH into the *Me ether* of the carbinol base, which is oxidised by *o*-C $_6$ H $_4$ (CO $_2$ H) $_2$  to 2:3-dimethoxyflavanone, m.p. 177°, hydrolysed by acid to the corresponding flavonol, m.p. 169°. H. W.

**Tetrahydrocannabinol analogues with marihuana activity.** XV. R. Adams, S. Loewe, C. W. Theobald, and C. M. Smith (*J. Amer. Chem. Soc.*, 1942, **64**, 2653—2655; cf. A., 1943, II, 69).—*m*-C $_6$ H $_4$ EtOH with H $_2$ -Raney Ni in EtOH at 200°/136 atm. gives 3-ethylcyclohexanol (89%), b.p. 96°/20 mm., 192.5—193°/748 mm. (3:5-dinitrobenzoate, m.p. 133—134°), oxidised by Na $_2$ Cr $_2$ O $_7$ -H $_2$ SO $_4$  to 3-ethylcyclohexanone (72%), b.p. 81°/12 mm. (semicarbazone, m.p. 166—167°; *p*-nitrophenylhydrazone, m.p. 128—129°), which with Et $_2$ C $_2$ O $_4$ -NaOEt etc. gives *Et* 5-ethylcyclohexanone-2-carboxylate (54%), b.p. 96—98°/2 mm. (2:4-dinitrophenylhydrazone, m.p. 122—122.5°). *Et* 5:5-, b.p. 125—128°/14 mm., 4:5-, b.p. 116°/10 mm., and 3:5-dimethylcyclohexanone-2-carboxylate, b.p. 103°/4 mm. (2:4-dinitrophenylhydrazones, m.p. 89°, 146—147°, and 175°, respectively), and cycloheptanone-2-carboxylate (14%), b.p. 77—79°/0.4 mm. [Cu salt, m.p. 193—194°; gives 1-phenyl-3:4-pentamethylene-5-pyrazolone, m.p. 207—210° (decomp.)], are similarly prepared. Standard methods lead to 3'-hydroxy-4'-ethyl-, m.p. 167—169°, -4':4'-, m.p. 190—190.5°, -4':5'-, m.p. 174.5—175.5°, and -4':6'-dimethyl-, m.p. 151.5—152.5°, -5'-*n*-amyl-3':4':5':6'-tetrahydrodibenz-2-pyrone and 5-hydroxy-7-*n*-amyl-3:4-pentamethylenecoumarin, m.p. 178.5—179°, which yield 3'-hydroxy-2:2-dimethyl-4'-ethyl- (I), b.p. 172°/0.1 mm., -2:2:4':4'- (II), m.p. 89—89.5°, -2:2:4':5'- (III), b.p. 181—182°/0.05 mm., and -2:2:4':6'-tetramethyl- (IV), b.p. 186°/0.05 mm., -4'-*n*-amyl-3':4':5':6'-tetrahydrodibenz-2-pyran and 5-hydroxy-2:2-dimethyl-7-*n*-amyl-3:4-pentamethylene-1:2-benzopyran (V), b.p. 180—182°/0.05 mm. Potencies relative to the 2:2:4'-Me $_3$  compound as unity are (I) 0.22, (II) 0.10, (III) 0.11, (IV) 0.75 (convulsant), and (V) 0.21, showing the depressing effect of variations in structure. M.p. are corr. R. S. C.

**Quinone dyes of the phenanthrofurane series.** III. Constitution of tanshinone II. F. von Wessely and T. Lauterbach (*Ber.*, 1942, **75**, [B], 958—970).—Tanshinone II (I) is probably A. Extraction of



the roots of *Salvia miltiorrhiza* with Et $_2$ O affords (I), C $_{15}$ H $_{12}$ O $_4$ , m.p. 216°, which is separated from tanshinone I (II) partly by crystallisation and partly by chromatography in C $_6$ H $_6$  over Al $_2$ O $_3$ . It does not contain OAlk. The presence of the *o*-quinonoid group is con-

firmed by the prep. of a quinoxaline derivative, C $_{25}$ H $_{22}$ ON $_2$ , m.p. 206°, by reduction (Pd sponge in EtOH) and subsequent methylation to leucotanshinone *Me* $_2$  ether (III), m.p. 92°, softens at 90°,  $[\alpha]_D^{25} \pm 0^\circ$  (picrate, m.p. 105—107°), and by reductive acetylation to the corresponding diacetate, m.p. 176°, softens at 172°. The third O of (I) is probably contained in a hetero-ring since (I) does

not react with Zerevitinov's or carbonyl reagents. Hydrogenation of (I) with a little Pd sponge in EtOH ceases with the absorption of 1 H $_2$  but with much Pd sponge in AcOH (I) and (III) fairly rapidly absorb 5 H $_2$  with partial loss of OMe in the case of (II). It is concluded that an aliphatic double linking is absent. Drastic oxidation of (I) by HNO $_3$  at 150° affords 1:2:3:4-C $_6$ H $_2$ (CO $_2$ H) $_4$  in excellent yield whereas the action of KMnO $_4$  in COMe $_2$  leads to a difficultly separable mixture of acids. With CrO $_3$  according to Kuhn-Roth (I) gives 1 mol. of AcOH whereas under less drastic conditions the product is an anhydride (III), C $_{14}$ H $_{14}$ O $_3$ , of an *o*-dicarboxylic acid, m.p. 136°, softens at 134°,  $[\alpha]_D^{25} \pm 0^\circ$  [corresponding acid, m.p. 196—198° (decomp.)]. Oxidation of (I) and (II) is similar in causing loss of 5 C and 4 H. The probable assumption that (I) contains a substituted furan ring is strengthened by the formation of (IV) by the ozonisation of (III). The same difference (CH $_6$ ) is observed between the mol. formula of (I) and (II) and those of their products of oxidation by CrO $_3$ . (IV) and CrO $_3$  (Kuhn-Roth) give 1/3 mol. of AcOH. 1:2:3:4-C $_6$ H $_2$ (CO $_2$ H) $_4$  is obtained in excellent yield by oxidation of (IV) with HNO $_3$ . Hydrogenation (Pd sponge in AcOH) of (IV) causes absorption of 3 H $_2$  and production of a non-homogeneous product from which a monocarboxylic acid, C $_{14}$ H $_{18}$ O $_2$ , m.p. 235°, is obtained; all the absorbed H appears to be required to convert 1 CO of (IV) into Me and since only 3 H $_2$  are similarly absorbed in presence of PtO $_2$  and AcOH it appears that an aliphatic double linking is not present in (IV). (IV) is therefore very probably the dicarboxylic anhydride of an alkylated tetrahydronaphthalene or indane. Thermal decomp. of the acid corresponding to (IV) gives a hydrocarbon resembling C $_{10}$ H $_7$ Me and yielding a picrate which could not be completely purified. (1:2:3:4-Tetrahydronaphthalene and its 1:1-Me $_2$  derivative are partly dehydrogenated when passed over heated Na $_2$ CO $_3$ .) Dehydrogenation of (IV) does not occur readily with K $_3$ Fe(CN) $_6$  in alkaline solution, with Pd sponge at 230°, or with heated Se. KMnO $_4$  in hot alkaline solution followed by treatment of the product (V) with CH $_2$ N $_2$  converts (IV) the *Me* $_3$  ester, C $_{14}$ H $_{16}$ O $_7$  (VI), m.p. 148—151°, which does not give AcOH (Kuhn-Roth), cannot be acetylated, does not react with carbonyl reagents, and does not yield CH $_4$  (Zerevitinov); the function of the seventh O is not determined. It is oxidised by HNO $_3$  to 1:2:3:4-C $_6$ H $_2$ (CO $_2$ H) $_4$ . (VI) is also obtained by esterification of (V) with HCl-MeOH but one CO $_2$ H reacts only with difficulty. H. W.

**Dioxanate of iodine pentafluoride.** A. F. Scott and J. F. Bunnett (*J. Amer. Chem. Soc.*, 1942, **64**, 2727).—IF $_5$  and dioxan give a 1:1 additive compound, m.p. 112° (decomp.; instantaneous), hydrolysed in air to HIO $_3$ . R. S. C.

**Diphenospiran derivative with constitutional relationships to the tocopherols.** P. Karrer and W. Fatzer (*Helv. Chim. Acta*, 1942, **25**, 1140—1143).—Passage of HCl into a solution of 3:6:2:4:1-(OH) $_2$ C $_6$ HMe $_2$ CHO and Me  $\beta$  $\zeta$  $\kappa$ -trimethyltridecyl ketone gives a blue pyrylium salt, C $_{36}$ H $_{51}$ O $_4$ Cl, (I) converted by NaOAc or NaHCO $_3$  in EtOH into 6:6'-dihydroxy-5:7:5':7'-tetramethyl-3'- $\gamma$  $\lambda$ -trimethyldodecyldiphenyl-2:2'-spiropyran, re-converted by HCl into (I). Catalytic reduction of (I) gives a liquid. H. W.

**Structure of indigoids.**—See A., 1943, I, 49.

**Basicity studies of tert. vinylamines.** R. Adams and J. E. Mahan (*J. Amer. Chem. Soc.*, 1942, **64**, 2588—2593).—Heterocyclic compounds containing endo- or exo-cyclic N:C:C are stronger bases than their saturated analogues, probably owing to equilibration of the former with the quaternary compounds, e.g.,

CH $_2$ <CH $_2$ :CH:CH $_2$ >NMe + H $_2$ O  $\rightleftharpoons$  CH $_2$ <CH $_2$ :CH:CH $_2$ >NMeOH. The following pK $_H$  (= pK $_{H_2O}$  - pK $_{ion}$ ) in H $_2$ O at 25° are recorded. 1:2-Dimethyl- 11.94, 1-methyl-2-*n*-butyl-, {b.p. 88.5°/30 mm.; 54% obtained from 1-methyl-2-pyrrolidone by MgBu $^a$ Br in Et $_2$ O-N $_2$  at room temp., with 14% of 1-methyl-2:2-di-*n*-butylpyrrolidine, b.p. 122°/18 mm. [methiodide, m.p. 211° (corr.)]} 11.90, 2-methyl-1-ethyl- [b.p. 73.5—74.5°/55 mm.; prep. from Br[CH $_2$ ] $_3$ ·COMe (I) by NH $_2$ Et-EtOH; 52%; unstable in air] 11.92, and 2-methyl-1-*n*-butyl- $\Delta^2$ -pyrroline [b.p. 82—83.5°/16 mm.; 39% from (I) by NH $_2$ Bu $^a$ -EtOH] 11.90 in 25% MeOH at 26°; 1:2-dimethyl- 10.26, 1-methyl-2-*n*-butyl- 10.24, 2-methyl-1-ethyl- 10.64, 2-methyl-1-*n*-butyl- 10.69, and 1-methyl-pyrrolidine 10.36; 1-methyl- $\Delta^3$ -pyrroline 9.92; 1:2-dimethyl- 10.26, 2-methyl-1-ethyl- 10.70, 1-propenyl- (b.p. 51—53°/10 mm.) 10.66 in 25% MeOH at 28°, 1-propyl- 10.48, 1-allyl- 9.69, 2-methyl- 10.99, and 1-*n*-butyl-piperidine 10.49; piperidine 11.12; NMe $_2$ ·[CH $_2$ ] $_4$ ·COMe 9.67; *n*-C $_6$ H $_{11}$ ·CH:CH·NMe $_2$  10.38 in 50% MeOH at 28°; *n*-C $_7$ H $_{15}$ ·NMe $_2$  9.94 in 50% MeOH at 26°; 1:1 piperidine-EtCHO in 25% MeOH 10.77 at 27°; 1:1 NH $_2$ Et-*n*-C $_6$ H $_{13}$ ·CHO in 50% MeOH 10.50 at 27°. Butyrolactone and NH $_2$ Bu $^a$  at 280° give 95% of 1-*n*-butyl-*n*-pyrrolidone, b.p. 121°/16 mm. The formula of lysergic acid (A., 1938, II, 463) needs revision. R. S. C.

**Anhydrides of basic amino-acids.** D. W. Adamson (*J.C.S.*, 1943, 39—40).—"*dl*-Lysine anhydride," obtained by heating *dl*-lysine Me ester dihydrochloride with NaOMe, contains 40% of *dl*-3-amino-homopiperidone (I), b.p. 167°/12 mm., m.p. 68—71° [hydrochloride, m.p. 294—296° (decomp.)]; picrate, darkens 215°, m.p. 233° (de-

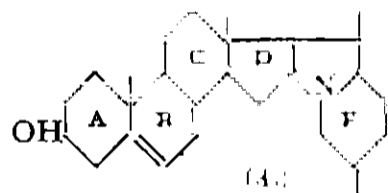
comp.): cf. Fischer *et al.*, A., 1905, i, 121]. *p*-NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Cl and **I** give 3-(*p*-acetamidobenzenesulphonamido)homopiperidine, m.p. 286—288° (decomp.), hydrolysed (HCl) to  $\epsilon$ -amino- $\alpha$ -(*p*-aminobenzenesulphonamido)-*n*-hexoic acid, m.p. 286° (decomp.). *d*-NH<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·CH(NH<sub>2</sub>)·CO<sub>2</sub>H·2HCl in MeOH with HCl affords 1-3-aminopyrrolidone, b.p. 175°/20 mm., m.p. 106—108°, [ $\alpha$ ]<sub>D</sub><sup>18</sup> -31.7° in H<sub>2</sub>O (hydrochloride, m.p. 198—200°; picrate, m.p. 185—187°; 3-Ac derivative, m.p. 176°), which similarly forms 3-(*p*-acetamidobenzenesulphonamido)pyrrolidone, m.p. 222—224° (decomp.), and  $\gamma$ -amino- $\alpha$ -(*p*-aminobenzenesulphonamido)-*n*-butyric acid, m.p. 259—260° (decomp.). F. R. S.

**Dihydropyridones.**—See B., 1943, II, 74.

**Compound formation between the isomeric hydroxydiphenyls and pyridine.**—See A., 1943, II, 88.

**Co-ordination tenacity of unsaturated molecules.** A. Gelman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 347—350).—The co-ordination tenacity of unsaturated mols. under normal conditions (not to be confused with the relative stability of the derived complexes) decreases in the order: NO > CO > CHPh:CH<sub>2</sub> > C<sub>4</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> > C<sub>3</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>8</sub>. In 3 days, CO displaces C<sub>3</sub>H<sub>6</sub> from C<sub>5</sub>H<sub>5</sub>N·H[PtCl<sub>3</sub>·C<sub>3</sub>H<sub>6</sub>] in H<sub>2</sub>O, to give C<sub>5</sub>H<sub>5</sub>N·H[PtCOCl<sub>3</sub>] (**I**), which with C<sub>5</sub>H<sub>5</sub>N affords Pt carbonylpyridinedichloride, [PtCO(C<sub>5</sub>H<sub>5</sub>N)Cl<sub>2</sub>] (**II**); substitution occurs similarly in the case of ethylene Zeise's salt, and this method is the best for preparing CO compounds of Pt. Neither C<sub>3</sub>H<sub>6</sub> nor C<sub>2</sub>H<sub>4</sub> displaces CO from (**II**). NO reacts slowly with the C<sub>2</sub>H<sub>4</sub> salt, and after 20 days, 50% of Pt nitrosylpyridine dichloride, [PtNO(C<sub>5</sub>H<sub>5</sub>N)Cl<sub>2</sub>], is formed, which is unchanged with an EtOH solution of CHPh:CH<sub>2</sub>. A slightly acid solution of C<sub>5</sub>H<sub>5</sub>N·H[PtCl<sub>3</sub>(CHPh:CH<sub>2</sub>)] with CO gives (**I**) (+H<sub>2</sub>O), convertible into (**II**). An acidified solution of (**I**) and NO (2 months) give a complex, (C<sub>5</sub>H<sub>5</sub>N·H)<sub>2</sub>PtCl<sub>6</sub>, also obtained from C<sub>5</sub>H<sub>5</sub>N, HCl and Na<sub>2</sub>PtCl<sub>6</sub>. Pt propylenepyridine dichloride, Pt(C<sub>3</sub>H<sub>6</sub>)(C<sub>5</sub>H<sub>5</sub>N)Cl<sub>2</sub>, dissolved in diallyl (**III**) affords a complex, [PtCl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)·C<sub>3</sub>H<sub>5</sub>]<sub>2</sub>; thus the co-ordination stability of (**III**) is > that of C<sub>3</sub>H<sub>8</sub>. (**III**) and [Pt(C<sub>2</sub>H<sub>4</sub>)NH<sub>3</sub>Cl<sub>2</sub>] give a complex, [(PtNH<sub>3</sub>Cl<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>10</sub>]. Attempts to make compounds with two or more unsaturated mols. failed. A. T. P.

**Steroids and sex hormones. LXXIX. 5-Methyl-2-ethylpyridine, a dehydrogenation product of solanidine.** V. Prelog and S. Szpilfogel [with E. Stahlberger] (*Helv. Chim. Acta*, 1942, **25**, 1306—1313).—Dehydrogenation of solanidine or solanidine (**I**) by Se in a sealed tube at 300—320° gives 5-methyl-2-ethylpyridine (**II**), characterised as the picrate, m.p. 143.5—144.5° or (indef.) 150—150.5°, and styphnate, m.p. 170° (decomp.). (**I**) is probably A. Et  $\beta$ -amino- $\Delta^5$ -pentenoate, b.p. 105°/13 mm., obtained by passing NH<sub>3</sub> into a mixture of NH<sub>4</sub>NO<sub>3</sub> and COEt·CH<sub>2</sub>·CO<sub>2</sub>Et in Et<sub>2</sub>O, is converted by CMeNa(CO<sub>2</sub>Et)<sub>2</sub> followed by HCl into 4:6-dihydroxy-



5-methyl-2-ethylpyridine, m.p. 238°, transformed by POCl<sub>3</sub> at 210° into the 4:6-Cl<sub>2</sub>-compound, b.p. 125—130°/12 mm., which is reduced (Raney Ni in MeOH containing NaOMe) to (**II**), b.p. 73—76° (bath)/12 mm. Analogously NH<sub>2</sub>·CMe·CH·CO<sub>2</sub>Et and CHMe(CO<sub>2</sub>Et)<sub>2</sub> afford 4:6-dihydroxy-, m.p. 276.5°, whence successively 4:6-dichloro-2:5-dimethylpyridine, b.p. 120° (bath)/12 mm., and 2:5-lutidine (picrate, m.p. 170.5°) result. M.p. are corr. H. W.

**Synthetic production of growth substances.** S. S. Nametkin and N. A. Dzbanovski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 330—332).—Syntheses of 3-indolyl-acetic (heteroauxin) and -butyric acid, and of  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·CH<sub>2</sub>·CO<sub>2</sub>H, are discussed. A. T. P.

**Synthesis of  $\gamma$ -3-indolylbutyric acid by a new procedure.** S. S. Nametkin, N. A. Dzbanovski, and A. G. Rudnev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 333—335).—Indole and MgEtI in PhOMe (not in Et<sub>2</sub>O) at 65—70° give C<sub>8</sub>H<sub>6</sub>N·MgI, converted by Cl·[CH<sub>2</sub>]<sub>3</sub>·CN in PhOMe, first cold and then at 120° for 1 hr. (mixture becomes red), into a complex, decomposed by cold aq. AcOH·C<sub>6</sub>H<sub>6</sub> to  $\gamma$ -3-indolyl-butyronitrile, which is hydrolysed by boiling 20% aq. KOH (8 hr.; yield 83.5%) to the -butyric acid (cf. Jackson *et al.*, A., 1931, 363). A. T. P.

**Solubilities and compositions of the phospho-12-tungstates of diamino-acids and of proline, glycine, and tryptophan.**—See A., 1943, II, 82.

**Nitration of lepidine and 2-chlorolepidine.** S. E. Krahler and A. Burger (*J. Amer. Chem. Soc.*, 1942, **64**, 2417—2419).—8-Nitro-lepidine (**I**) and Br give 8-nitro-4-dibromomethylquinoline (89%), m.p. 111.5—112.5°, hydrolysed by AgNO<sub>3</sub> in 60% AcOH at 100° to 8-nitroquinoline-4-aldehyde (**II**) (97%), m.p. 163—173°, which is obtained less well from (**I**) by SeO<sub>2</sub>. KMnO<sub>4</sub>·COMe<sub>2</sub>·H<sub>2</sub>O at 40° converts (**II**) into 8-nitrocinchonic acid (71%), m.p. 253—254° (decomp.), which, when heated with Cu-bronze at 100 mm., gives 8-nitroquinoline. 2-Chlorolepidine (**III**) and Br in NaOAc·AcOH give 2-hydroxy-4-dibromomethylquinoline (12%), m.p. 307—308° (decomp.), whence the aldehyde could not be obtained. Condensation of *o*-C<sub>6</sub>H<sub>4</sub>Cl·NO<sub>2</sub>, CH<sub>2</sub>Ac·CO<sub>2</sub>Et, and a trace of HCl over

H<sub>2</sub>SO<sub>4</sub> in vac. and then heating in paraffin at 240° gives 8-chloro-4-hydroxyquinoline (**IV**) (29%), m.p. 229—230°, converted by POCl<sub>3</sub> at 100° into 4:8-dichloroquinoline (**V**) (85%), m.p. 87—88° (with Zn dust gives quinoline). With boiling piperidine, (**V**) gives 8-chloro-4-piperidino- (**VI**), m.p. 124—125° (picrate, m.p. 161—163°), and with boiling NaOMe·MeOH gives 8-chloro-4-methoxyquinoline (**VII**), m.p. 122—124°. The product previously (A., 1942, II, 36) believed to be 2-chloro-5-nitrolepidine is the 8-NO<sub>2</sub>-compound (cf. A., 1942, II, 150). The 8-chlorolepidine compounds of Kermack *et al.* (A., 1933, 513) are the quinoline derivatives (**IV**)—(**VII**). With CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>·NaOEt·EtOH and then KOH·EtOH, (**III**) gives only 2-ethoxylepidine. The prep. of 2-keto-4-methyl-1:2-dihydroquinoline-1:8-diazoimide, m.p. 236—237.5°, is improved; in boiling EtOH it gives 2-hydroxylepidine and MeCHO. R. S. C.

**Reaction between halogen derivatives of 6-methoxyquinoline and alkoxides.** A. M. Berkenheim and L. V. Antik (*J. Gen. Chem. Russ.*, 1941, **11**, 537—540).—7-Bromo-6-methoxyquinoline (**I**), m.p. 110—111° (prepared by Skraup's reaction from 4:2:1-NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·Br·OMe), when heated with ONa·[CH<sub>2</sub>]<sub>2</sub>·NEt<sub>2</sub> (**II**) for 5.5 hr. at 120—180°, gives 6-methoxyquinoline, instead of the expected 6-methoxy-7- $\beta$ -diethylaminoethoxyquinoline. 7-Bromo-6-ethoxyquinoline, m.p. 89—90° (Skraup synthesis), 8-bromo-6-methoxyquinoline, m.p. 65—66° (Sandmeyer reaction, from 8-amino-6-methoxyquinoline), and 8-iodo-6-ethoxyquinoline react in the same way as (**I**) with (**II**) or NaOEt. R. T.

**Condensation of S-hydroxy-6-methoxyquinoline with  $\gamma$ -halogeno- $\alpha$ -diethylaminopropane.** A. M. Berkenheim and N. S. Spasokotski (*J. Gen. Chem. Russ.*, 1941, **11**, 541—544).—6:8-Dihydroxyquinoline and NaOEt in EtOH with *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>Me yield 8-hydroxy-6-methoxyquinoline, the Na salt of which condenses with NEt<sub>2</sub>·[CH<sub>2</sub>]<sub>3</sub>·Cl in EtOH (5 hr. at 50°) to 6-methoxy-8- $\gamma$ -diethylaminopropoxyquinoline, b.p. 198—200°/1—1.25 mm. This does not exhibit any anti-malarial properties. R. T.

**Condensation reactions of isoquinoline-1-aldehyde.** R. S. Barrows and H. G. Lindwall (*J. Amer. Chem. Soc.*, 1942, **64**, 2430—2432).—1-Methylisoquinoline (prep. from the 3:4-H<sub>2</sub>-derivative by boiling with Raney Ni; 70—75% yield) with SeO<sub>2</sub> in warm dioxan (later at 100°) gives isoquinoline-1-aldehyde (42%), m.p. 55—55.5° (reduces Tollens' reagent; adds NaHSO<sub>3</sub>; semicarbazone, m.p. 195—197°; oxime, m.p. 171—172°; phenylhydrazone, m.p. 174—175°). With MeNO<sub>2</sub> and NHET<sub>2</sub> (2 drops) this gives 1- $\beta$ -nitro- $\alpha$ -hydroxyethylisoquinoline (71%), m.p. ~106—107°; with CPhMe-alkali gives, according to the conditions,  $\beta$ -hydroxy- $\beta$ -1-isoquinolylpropiophenone (85%), m.p. 114.5—115°,  $\beta$ -1-isoquinolylacrylophenone (60—77%), m.p. 145.5—146°, or  $\alpha$ -diphenyl- $\gamma$ -1-isoquinolyl-*n*-pentane- $\alpha$ -dione (42%), m.p. 133—133.5°; with CH<sub>2</sub>Ph·CN·NaOEt·EtOH gives  $\alpha$ -phenyl- $\beta$ -1-isoquinolylacrylonitrile (92%), m.p. 96.5—97°, and with CH<sub>2</sub>Ph·CO<sub>2</sub>Et·NaOEt·EtOH gives Et  $\beta$ -hydroxy- $\alpha$ -phenyl- $\beta$ -1-isoquinolylpropionate (45%), m.p. 134.5—135.5°; Perkin condensation with CH<sub>2</sub>Ph·CO<sub>2</sub>H does not occur. 1:3-Dimethyl-6:7-methylenedioxyisoquinoline and SeO<sub>2</sub> in dioxan give (?) 3-methyl-6:7-methylenedioxyisoquinoline-1-aldehyde (34%), m.p. 186.5—188.5° (oxime, m.p. 215—216°). R. S. C.

**Deamination of 8-nitro-5-aminoisoquinoline.** B. Keilin and W. E. Cass (*J. Amer. Chem. Soc.*, 1942, **64**, 2442—2444).—5-Acetamidoisoquinoline with KNO<sub>3</sub>·H<sub>2</sub>SO<sub>4</sub> at 15—20° gives the 8-NO<sub>2</sub>-derivative (71%), m.p. 226—228°, hydrolysed by conc. HCl to 8-nitro-5-aminoisoquinoline (97%), m.p. 268—270° (decomp.) [hydrochloride, +H<sub>2</sub>O and anhyd., m.p. 289—291° (decomp.)], which with NaNO<sub>2</sub>·HCl at -10° to 0° and then H<sub>3</sub>PO<sub>2</sub> gives 8-chloroisoquinoline (**I**) (70%), new m.p. 55.5—56.5° (picrate, m.p. 189.5—191.5°). Et<sub>2</sub> *o*-chlorobenzylideneaminoacetal, b.p. 114—117°/2 mm., with P<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>SO<sub>4</sub> gives 9% of (**I**). M.p. are corr. R. S. C.

**Reaction of carbazole with malonic esters to 1:9-malonylcarbazoles.** P. Baumgarten and M. Riedel (*Ber.*, 1942, **75**, [B], 984—986).—Thermal condensation of NH<sub>2</sub>Ph with CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> under different conditions, alone or in the presence of PhNO<sub>2</sub>, paraffin, or *n*-C<sub>12</sub>H<sub>25</sub>·OH or under the influence of NaOEt, or decomp. by heat of CH<sub>2</sub>(CO·NHPh)<sub>2</sub> does not give substituted quinolines, which are readily derived from NH<sub>2</sub>Ph and CHR(CO<sub>2</sub>Et)<sub>2</sub> (R = aryl or Et). Analogously NHPh<sub>2</sub> and CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> at ~240° give 2:4-diketo-1-phenyl-1:2:3:4-tetrahydroquinoline, m.p. ~300° (decomp.), in ~80% yield. Indole is not reactive. Carbazole does not react with CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>, CH<sub>2</sub>(CO·NH<sub>2</sub>)<sub>2</sub>, or CH<sub>2</sub>(COCl)<sub>2</sub>, but is transformed by CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> at 270—280° into 1:9-ethylmalonylcarbazole (**I**), m.p. 257—258°. 1:9-Phenylmalonylcarbazole, m.p. 207—208°, is obtained similarly. (**I**) is oxidised by KMnO<sub>4</sub> to carbazole-1-carboxylic acid, m.p. 270—271°. Reduction (Clemmensen) of (**I**) affords 1( $\beta$ ):9- $\alpha$ -ethylacryloylenecarbazone, m.p. 128—129°, oxidised (KMnO<sub>4</sub> in COMe<sub>2</sub> at room temp.) to (**I**). H. W.

**Chemotherapeutic search for antimalarials. I. Synthesis of 1-amino-3-methoxy- and 8-chloro-1-amino-3-methoxy-acridine.** B. V. Samant (*Ber.*, 1942, **75**, [B], 1008—1015).—*m*-Nitro-*p*-anisidine is converted by diazotisation and subsequent boiling with H<sub>2</sub>O containing CuSO<sub>4</sub>, NaBr, and Cu wool into 4-bromo-3-nitroanisole, b.p. 153—154°/13 mm., m.p. 32°, which condenses with

$o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ ,  $\text{Na}_2\text{CO}_3$ , and reduced Cu in boiling 4-methylcyclohexanol to 2'-nitro-4'-methoxydiphenylamine-2-carboxylic acid (I), m.p. 228—230° (decomp.), and with 4-chloroanthranilic acid, m.p. 231° (obtained from 2 : 4 : 1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CO}_2\text{H}$ , 37%  $\text{NH}_3$ , and freshly reduced Cu at 120°), to 5-chloro-2'-nitro-4-methoxydiphenylamine-2-carboxylic acid (II), m.p. 268—271° (decomp.). When boiled with  $\text{POCl}_3$  (I) gives 5-chloro-1-nitro-3-methoxyacridine, m.p. 205—206° (decomp.), whilst (II) yields 5 : 8-dichloro-1-nitro-3-methoxyacridine, m.p. 270—271° (decomp.). When treated successively with  $\text{POCl}_3$  and 25% aq.  $\text{NH}_3$  (I) affords 1-nitro-3-methoxyacridone, m.p. 236°, and (II) gives 8-chloro-1-nitro-3-methoxyacridone, m.p. 277—278° (decomp.). These are reduced ( $\text{SnCl}_2$ ) to 1-amino-3-methoxyacridone, m.p. 254—256° (decomp.), and 8-chloro-1-amino-3-methoxyacridone, decomp. 287—293°, respectively, which are converted ( $\text{Na-Hg}$ ) into 1-amino-3-methoxyacridine, m.p. 135—136° [monohydrochloride, m.p. 254—256° (decomp.); monopicrate, m.p. 201—203° (decomp.); monomethiodide, m.p. 211—212° (decomp.)], and 8-chloro-1-amino-3-methoxyacridine, m.p. 191° [monohydrochloride, m.p. 237—238° (decomp.)]. *Me* 2 : 4-dichlorobenzoate, b.p. 132°/15 mm., is incidentally described. H. W.

**Preparation and therapeutic properties of certain acridine derivatives. III. 5-Styrylacridines and their quaternary salts.** W. Sharp, (Miss) M. M. J. Sutherland, and F. J. Wilson (*J.C.S.*, 1943, 5—7).—5-Methylacridine (I) (metho-*p*-toluenesulphonate, m.p. 204°) and  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  give  $\alpha$ -(*o*-nitrophenyl)- $\beta$ -(5-acridyl)ethanol, m.p. 177°. *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  and (I) with  $\text{ZnCl}_2$  afford 5-*m*-nitrostyrylacridine (II), m.p. 210°, and without  $\text{ZnCl}_2$ ,  $\alpha$ -(*m*-nitrophenyl)- $\beta$ -(5-acridyl)ethanol, m.p. 145°, and an isomeride (*cis-trans*?) of (II), m.p. 207°, are obtained. Reduction of (II) yields 5-*m*-aminostyrylacridine, m.p. 234° (lit. 232—234°); the *Ac* derivative, m.p. 252°, can be converted into the methochloride, decomp. >200°. Similarly, with  $\text{ZnCl}_2$  (I) and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  give 5-nitrostyrylacridine, m.p. 293° (Br-substitution product, m.p. >360°), and without  $\text{ZnCl}_2$ ,  $\alpha$ -(*p*-nitrophenyl)- $\beta$ -(5-acridyl)ethanol, m.p. 174°, is formed in addition. 5-*p*-Aminostyrylacridine, m.p. 242° (lit. 209°), yields an *Ac* derivative, m.p. 263°, whence the methochloride hydrochloride, decomp. ~250°. 5-*p*-Dimethylaminostyrylacridine methochloride, decomp. >200°, is also described. These results do not agree entirely with those obtained by Porai-Koschitz *et al.* (*A.*, 1907, i, 974).

F. R. S.

**Complex formation between iodine and  $\mu$ -thiodihydroglyoxalines.** T. B. Johnson and C. O. Edens (*J. Amer. Chem. Soc.*, 1942, 64, 2706—2708).—2-Thiol-4 : 5-dihydroglyoxaline (I) [prep. from  $(\text{CH}_2\cdot\text{NH}_2)_2$  with  $\text{CS}_2$  and then conc.  $\text{HCl}$  at 100°] absorbs 6 I in aq. KI at room temp. to give bis-4 : 5-dihydro-2-glyoxalanyl disulphide and therefrom the additive compound (II),  $\text{C}_6\text{H}_{10}\text{N}_4\text{S}_2\text{HI}_2\text{I}_2$ , m.p. 119°. The periodide (III),  $\text{C}_6\text{H}_{14}\text{N}_4\text{S}_2\text{HI}_2\text{I}_2$ , m.p. 67°, of di-4-methyl-4 : 5-dihydro-2-glyoxalanyl disulphide is similarly obtained from 2-thio-4-methyl-4 : 5-dihydroglyoxaline [prep. as (I)], m.p. 100°. In boiling  $\text{H}_2\text{O}$ , (II) gives di-4 : 5-dihydro-2-glyoxalanyl sulphide hydriodide (IV), I, and  $\text{H}_2\text{SO}_4$ ; by this method (III) gives only an oil. With aq.  $\text{NH}_3$ , (II) gives exothermally, *inter alia*, (I) and  $\text{NH}_4\text{I}$ .  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  and (I) in boiling  $\text{H}_2\text{O}$  give 4 : 5-dihydro-2-glyoxalanylthiolacetic acid, m.p. 223° (decomp.). With I-KI- $\text{H}_2\text{O}$ , (IV) gives a periodide,  $\text{C}_6\text{H}_{10}\text{N}_4\text{S}_2\text{HI}_2\text{I}_2$ , m.p. 170—175°, converted at 125° into (IV) and I. 5-Methyl-4 : 5-dihydro-2-glyoxalanylthiolacetic acid, m.p. 215°, is prepared as above, but (IV) gives only its hydrochloride. 2-Thiol-5-methylglyoxaline with I-KI- $\text{H}_2\text{O}$  gives di-5-methyl-2-glyoxalanyl disulphide periodide,  $\text{C}_8\text{H}_{10}\text{N}_4\text{S}_2\text{HI}_2\text{I}_2$ , cryst., decomp. when heated.

R. S. C.

**Ultra-violet absorption spectra and structure of *N*-phenylpyrazolone derivatives. IV. General survey of spectra and structure in relation to pharmacodynamic action.** N. A. Valjaschko and V. I. Blizniukov (*J. Gen. Chem. Russ.*, 1941, 11, 559—566).—Antipyrine (I) and pyrazolone (II) are complex mesomeric systems, of which those having the hydrazo- and diazo-structures of  $\text{NHPh}\cdot\text{NH}_2$  (III) predominate; the pharmacodynamic action of (I) and (II) is connected with these structures. The lower toxicity of (I) and (II) as compared with (III) is ascribed to resonance in the pyrazolone ring, which causes reduced lability of the electrons of the N atoms. The effect of substituting a 2-Me or a 4-NMe<sub>2</sub>-group into the pyrazolone ring is still further to favour the above structures as compared with (III).

R. T.

**Iminazolines.**—See B., 1943, II, 76.

**I-Carbamyl-5-methylpyrazole-3-carboxylic acid.** A. L. Lehninger (*J. Amer. Chem. Soc.*, 1942, 64, 2507—2508).— $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  and  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$  in warm  $\text{H}_2\text{O}$  give 1-carbamyl-5-methylpyrazole-3-carboxylic acid (80—85%), decomp. from 155°, m.p. 232—234° (corr.) (cf. von Auwers *et al.*, *A.*, 1930, 789), from which the  $\text{CO}\cdot\text{NH}_2$  is removed by boiling with  $\text{H}_2\text{O}$ .

R. S. C.

**Hydrolysis of acetylsulphanilic acid derivatives. III.** S. I. Lurie, O. I. Starobogatov, and E. S. Nikitskaja (*J. Gen. Chem. Russ.*, 1941, 11, 545—549).—The Ag salt of 2-methylglyoxaline (I) and *p*-NHAc- $\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$  (II) in EtOH (1.5 hr. at the b.p.) yield 1-*p*-acetamidobenzenesulphonyl-2-methylglyoxaline, m.p. 93—94.5°, readily hydrolysed with production of *p*-NH<sub>2</sub>- $\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$  by HCl in aq. EtOH

(30 min. at the b.p.).  $\beta$ -Bromoethylphthalimide and (I) in xylene (6 hr. at the b.p.) yield  $\beta$ -(2'-methyl-1'-glyoxalanyl)ethylphthalimide, m.p. 161—162°. This is heated with  $\text{N}_2\text{H}_4$  in EtOH (30 min. at the b.p.), 10% HCl is added, and boiling is continued for a further 90 min., affording  $\beta$ -(2'-methyl-1'-glyoxalanyl)ethylamine dihydrochloride, m.p. 196—198°, which, condensed with (II) in aq.  $\text{COMe}_2$ , gives the corresponding *N*-acetylsulphanilamide, m.p. 212—214°, hydrolysed by HCl in aq. EtOH to the  $\beta$ -(2'-methyl-1'-glyoxalanyl)ethylamide of sulphanilic acid. 4-Amino-2-phenylquinoline (III) and (II) in  $\text{C}_5\text{H}_5\text{N}$  (15 min. at the b.p.) yield the 2'-phenyl-4'-quinolylamide of *N*-acetylsulphanilic acid, m.p. 269—270°, hydrolysed as above to *p*-NH<sub>2</sub>- $\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$  and (III).

R. T.

**Ultra-violet absorption spectra of barbituric acid derivatives. III. Ionisation and 5-monosubstituted barbituric acid derivatives. IV. 5 : 5-Disubstituted barbituric acid derivatives.** R. E. Stuckey (*Quart. J. Pharm.*, 1942, 15, 370—376, 377—383).—III. The increase in the absorption (*A.*, 1941, II, 148) of barbituric acid (I) on dilution follows the increase in the degree of ionisation. The spectra of 5-methyl- (II), m.p. 205—207°, and 1 : 5-dimethyl-barbituric acid (III), m.p. 171—172° [from  $\text{CHMe}(\text{CO}_2\text{Et})_2$ ,  $\text{NH}_2\cdot\text{CO}\cdot\text{NHMe}$ , and EtOH-NaOEt], in aq. acid and alkali are similar to those of (I). Oxidation ( $\text{H}_2\text{O}_2$ ) or evaporation of aq. solutions of (II) and (III) gives 5-hydroxy-5-methyl-, m.p. 225—227°, and 5-hydroxy-1 : 5-dimethyl-barbituric, m.p. 166—167°, respectively. 1 : 3 : 5-Trimethyl-barbituric acid could not be prepared from  $\text{CHMe}(\text{CO}_2\text{Et})_2$  and  $\text{CO}(\text{NHMe})_2$ .

IV. 5 : 5-Disubstituted barbituric acids in general show a peak in alkaline solution at ~2500 Å. and thereby allow the determination of small amounts (if known) in extracts etc. 5 : 5-Dimethyl-barbituric acid is anomalous and presumably forms a stable keto ion; differences in other properties are noted. 1 : 5 : 5-Trimethyl-barbituric acid (from Ag 1-methylbarbiturate and MeOH-MeI) also shows only end absorption in both acid and alkali. The 1 : 3 : 5 : 5-Me<sub>4</sub> compound resembles other derivatives methylated in the 1- and 3-positions.

H. B.

***N*-Aralkylbarbituric acids.** A. Ardis, J. S. Buck, and R. Baltzly (*J. Amer. Chem. Soc.*, 1942, 64, 2514).—1-Benzyl-, m.p. 64°, and 1- $\beta$ -phenylethyl-, m.p. 74°, -5-ethyl-5-*n*-butylbarbituric acid and 1-benzyl-, m.p. 87—88°, and 1- $\beta$ -phenylethyl-, m.p. 106—107°, -5-ethyl-5-isoamylbarbituric acid are prepared.

R. S. C.

**Chemotherapy of bacterial infections. VII. Synthesis of sulphanilamide derivatives of the pyrimidine group.** K. Ganapathi, C. V. Deliwala, and M. V. Shirsat (*Proc. Indian Acad. Sci.*, 1942, A, 16, 115—125; cf. *A.*, 1941, II, 338).—Addition of a mixture of  $\text{HCO}_2\text{Et}$  and EtOAc to powdered Na in dry Et<sub>2</sub>O at 0° and treatment of the product after remaining overnight at room temp. with sulphanilylguanidine (I) and NaOEt in EtOH gives 2-sulphanilamidopyrimidone (II), m.p. 268—269°, in 50—60% yield. Successive additions of (I) and  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  or its  $\alpha$ -alkyl derivatives to NaOEt in EtOH and boiling of the mixture lead to the following 2-sulphanilamido-4-methyl-5-alkylpyrimidones in which the alkyl is represented by H, m.p. 253—254°, *Me*, m.p. 238—239°, *Et*, m.p. 208—209°, *Bu*<sup>a</sup>, m.p. 121—122°, isoamyl, m.p. 190—193°, and *n*- $\text{C}_6\text{H}_{13}$ , m.p. 108—110°. 2-Acetsulphanilamido-4-methyl- (III), m.p. 273°, and -isoamyl, m.p. 228—229°, -pyrimidone are obtained similarly. 2-Sulphanilamido-4-methylpyrimidone (IV) is considerably resistant to boiling 3*N*-HCl but suffers some hydrolysis when boiled for ~6 hr. with 37% HCl; 2-amino-4-methylpyrimidone results but  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$  could not be isolated. (IV) appears indifferent towards 30% NaOH. (IV),  $\text{Me}_2\text{SO}_4$ , and aq. NaOH in boiling  $\text{COMe}_2$  yield 2-sulphanilylmethylamido-1 : 4-dimethylpyrimidone, m.p. 160—165° after shrinking. (III) and boiling  $\text{POCl}_3$  yield the compound,  $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}_4\text{ClS}$ , m.p. >280°, which does not give a halogen-free compound when boiled with Zn dust and  $\text{H}_2\text{O}$ . 2-Amino-4-methylpyrimidone is transformed by NaOH and  $\text{Me}_2\text{SO}_4$  into 2-amino-1 : 4-dimethylpyrimidone, m.p. >280°, which when dissolved in NaOH and treated with  $\text{NaHCO}_3$ , *p*-NH<sub>2</sub>- $\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ , and  $\text{COMe}_2$  affords 2'-amino-4'-methyl-6'-pyrimidonyl *p*-acetamidobenzenesulphonate, m.p. 193—194°. Acetsulphanilylguanidine and mesityl oxide (V) in boiling abs. EtOH containing NaOEt give 2-sulphanilylimido-4 : 4 : 6-trimethyl-2 : 3 : 4 : 5-tetrahydropyrimidine (VI), m.p. 190—193° (*Ac* derivative, m.p. 241—242°), and 2-sulphanilamido-4 : 4 : 6-trimethyl-4 : 5-dihydropyrimidine, m.p. 228—230° (*Ac* derivative, m.p. 217—218°). In different experiments compounds,  $\text{C}_{13}\text{H}_{18}\text{O}_2\text{N}_4\text{S}$ , m.p. 130—135° and 190—193°, respectively, were obtained from (I) and (V). (II), (V), and (VI) are devoid of therapeutic activity.

H. W.

***N*<sup>1</sup>-Sulphanilamidoalkylpyrimidines.** G. W. Raiziss and M. Freifelder (*J. Amer. Chem. Soc.*, 1942, 64, 2340—2342).—*p*-NHAc- $\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$  and the appropriate aminopyrimidine in  $\text{C}_5\text{H}_5\text{N}$  at 60° give 55—95% of 2-*N*<sup>1</sup>-acetylsulphanilamido-4-methyl-, m.p. 244°, -4-ethyl-, m.p. 274°, -4-*n*-propyl-, m.p. 258°, -4-isobutyl-, m.p. 233°, -4-*n*-amyl-, m.p. 222—223°, -4-hexyl-, m.p. 216°, -4 : 5-dimethyl-, m.p. 272—273°, -5-methyl-4-ethyl-, m.p. 286°, and -4-phenyl-, m.p. 287°, -pyrimidine, 2-*N*<sup>1</sup>-acetylsulphanilamido-5 : 6 : 7 : 8-tetrahydroquinazoline, m.p. 259°, and 2 : 5-di-*N*<sup>1</sup>-acetylsulphanilamido-pyrimidine, m.p. 295° (decomp.), hydrolysed by boiling 5%

NaOH to the corresponding  $p$ -NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH-compounds (40—60% yield), m.p. 235—236°, 242°, 212—214°, 232°, 226°, 204°, 222°, 215°, 264°, 247°, and 241—242°, respectively. The 4:5-Me<sub>2</sub> and 4-Me compounds have good antipneumococcal (type II) activity [in fact, the Et derivative slight activity, but the others none]. NH<sub>2</sub>C(NH<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>CO<sub>3</sub> with ONa·CH<sub>2</sub>·CH·COR in MeOH gives 2-amino-4-isobutyl-, m.p. 119°, -4-*n*-amyl-, m.p. 90°, and -5-methyl-4-ethyl-, m.p. 157°, -pyrimidine. 2-Amino-4-hexylpyrimidine, obtained from COMe·C<sub>6</sub>H<sub>13</sub>-*n*, has m.p. 92—93° (cf. A., 1941, II, 377; 1942, II, 151) and is oxidised by HNO<sub>3</sub> to 2-amino-5-*n*-amylpyrimidine-4-carboxylic acid. (I) does not condense with isocytosine, divicine, or purines such as adenine or guanine.

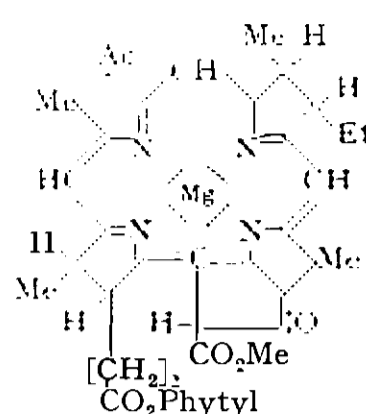
R. S. C.

**Synthesis of aminobenzoylenecarbamides and of dihydroxyquinoxalines isomeric with "luminol."** E. H. Huntress and (Miss) J. V. K. Gladding (*J. Amer. Chem. Soc.*, 1942, **64**, 2644—2649).—Analogues of luminol differing therefrom in arrangement of the CO and NH in the heterocyclic ring are not chemiluminescent when oxidised [H<sub>2</sub>O<sub>2</sub>—K<sub>3</sub>Fe(CN)<sub>6</sub>]. 6:2:1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)·CO<sub>2</sub>H (I) with KCNO—AcOH in H<sub>2</sub>O and then NaOH at 40° gives 5-nitro-2:4-dihydroxyquinazoline (67%), m.p. 357—358° (sealed tube), sol. in alkali, and converted by Me<sub>2</sub>SO<sub>4</sub>—5% KOH into the 1:3-Me<sub>2</sub> ether (77%), m.p. 275—277°. 2:4-Dihydroxyquinazoline with fuming HNO<sub>3</sub>—H<sub>2</sub>SO<sub>4</sub> gives the 6-NO<sub>2</sub>-derivative (86%), m.p. 331—332° (Me<sub>2</sub> ether, m.p. 213—214°). 4:2:1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)·CO<sub>2</sub>H with CO(NH<sub>2</sub>)<sub>2</sub> at 200° gives 7-nitro-2:4-dihydroxyquinazoline (76%), m.p. 337° (decomp.) [K salt; Me<sub>2</sub> ether, m.p. 229—230° (uncorr.)], and some amide. 3:2:1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)·CO<sub>2</sub>H (II) and CO(NH<sub>2</sub>)<sub>2</sub> at 180—190° give 8-nitro-2:4-dihydroxyquinazoline (III) (68%), m.p. 272—273° (sealed tube) [with conc. HNO<sub>3</sub>—H<sub>2</sub>SO<sub>4</sub> at 100° gives the 6:8-(NO<sub>2</sub>)<sub>2</sub>-compound, m.p. 263—265° (uncorr.); Me<sub>2</sub> ether, m.p. 217—218°], and some 3-nitro-2-aminobenzamide, m.p. 234—235° [hydrolysed to (II), m.p. 267—268° (decomp.)]; with CO(NH<sub>2</sub>)<sub>2</sub> at 200° gives (III)]. (II) is obtained by the reactions, (a) 3:1:2-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me·NHAc → (neutral KMnO<sub>4</sub>) 3:2:1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(NHAc)·CO<sub>2</sub>H (74%) → (II) (87%), and (b) 3:2:1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>O → (aq. NH<sub>3</sub>) 3:1:2-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>H)·CO·NH<sub>2</sub> (70%) → (Hofmann) (II) (90%). (I) is prepared thus: 3:2:1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>NH<sub>4</sub>)<sub>2</sub> → (at 235—250°) 3:2:1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>NH (94%) → (0.5N-NaOH) 6:1:2-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>H)·CO·NH<sub>2</sub> (76%) → (Hofmann) (I) (90%). 5-, m.p. 295° (decomp.; sealed tube), 6-, decomp. >330°, 7-, m.p. >350°, and 8-amino-2:4-dihydroxyquinazoline, m.p. 279—281° (decomp.), are prepared from the NO<sub>2</sub>-compounds by SnCl<sub>2</sub>—HCl. 3:1:2-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)<sub>2</sub> and Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> at the b.p. give 5-nitro- (60%), m.p. 295° (decomp.; sealed tube), and thence (aq. Na<sub>2</sub>S) 5-amino-2:3-dihydroxyquinoxaline (44%), m.p. 344° (uncorr.; sealed tube). 4:1:2-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)<sub>2</sub> and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> at 150°, later 180—200°, give 6-nitro- (73%), m.p. 343—344° (decomp.; sealed tube), and thence 6-amino-2:3-dihydroxyquinoxaline (75%), decomp. ~330°, m.p. >350°. Unless otherwise stated, m.p. are corr. (block).

R. S. C.

**Bacteriochlorophyll. III.** H. Mittenzwei (*Z. physiol. Chem.*, 1942, **275**, 93—121; cf. Fischer *et al.*, A., 1938, II, 297).—Further confirmation of the fine structure of dehydrobacteriophæophorbide and chlorophyll *a* is found in the identity of the phytol from bacteriophæophytin with that of stinging nettles now established by means of the Ag salt of the corresponding phthalate. Also the oxime of "natural" 2-acetylchlorin *e*<sub>6</sub> is identical with that from the synthetic material. Natural 2-acetylmethylphæophorbide is smoothly converted by methanolysis into 2-acetylchlorin *e*<sub>6</sub> Me<sub>3</sub> ester. Ring-closure of bacteriochlorin *e*<sub>6</sub> Me<sub>3</sub> ester (I) to bacteriomethylphæophorbide (II), m.p. 260°, is effected with some difficulty by KOMe—MeOH in boiling C<sub>5</sub>H<sub>5</sub>N or by NaOMe—MeOH in COMe<sub>2</sub>. Optical activity of the bacterio-substances can be observed by use of white light but the vals. are influenced to an unusual extent by the presence of small amounts of impurity. (II) is not satisfactorily hydrogenated directly, with Pd—tetrahydronaphthalene or Pd—HCO<sub>2</sub>H, but is transformed by Al(OPr<sup>i</sup>)<sub>3</sub> into bacterio-2-deacetyl-2- $\alpha$ -hydroxymesomethylphæophorbide, which could not be caused to crystallise but passes in a high vac. into bacterio-2-deacetyl-2-vinylmethylphæophorbide. Similar reduction of (I) to non-cryst. bacterio-2-deacetyl-2- $\alpha$ -hydroxymesochlorin *e*<sub>6</sub> Me<sub>3</sub> ester, softens at 128°, proceeds more readily and does not cause loss of the "bacterio" type of spectrum. It loses H<sub>2</sub>O at ~200°. A cryst. Ac derivative could not be prepared but the structure of the compound is established by its re-oxidation by KMnO<sub>4</sub> in C<sub>5</sub>H<sub>5</sub>N to (I). In a high vac. it passes into bacterio-2-deacetyl-2-vinylchlorin *e*<sub>6</sub> Me<sub>3</sub> ester (III), m.p. 240—241°, with only small amounts of chlorin *e*<sub>6</sub> and 2- $\alpha$ -hydroxychlorin *e*<sub>6</sub>. (III) can be catalytically hydrogenated to the 2-Et compound (IV), which adds CHN<sub>2</sub>·CO<sub>2</sub>Et, but the change is not quant. and the ultimate evidence of the presence of CH<sub>2</sub>·CH· is afforded by dehydrogenation with *p*-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>·O. Oxidation of (I) or (II) by CrO<sub>3</sub>—H<sub>2</sub>SO<sub>4</sub> gives no methylethylmaleimide (V) but only small amounts of a colourless liquid. The same result is obtained by the oxidation of (III), whereas 2-acetylchlorin *e*<sub>6</sub> Me<sub>3</sub> ester affords (V). These observations can only be explained by the assumption that the "superfluous" H atoms of the bacterio-series are attached to nucleus II particularly since (IV) gives (V) which can only proceed

from nucleus I. Products of the oxidative fission of nucleus III have never been unquestionably isolated. The most important evidence in favour of the position of the "superfluous" H atoms



in nucleus II is obtained by the optical examination of the basic products of fission of the bacterio-derivatives. The oil is strongly dextrorotatory and most probably consists of *d*- $\alpha$ -methyl- $\alpha'$ -ethylsuccinic anhydride, so that the H atoms in the  $\alpha\alpha'$  positions are already present in the initial material. The acid fractions of the oxidation of the chlorophyll *a*, 2-acetyl-, and bacterio-series invariably give a colourless, laevorotatory liquid which appears to be a hæmotricarboxylimide; nucleus IV is therefore similar in all derivatives of the chlorophyll and bacteriochlorophyll (VI) series. The annexed structure is proposed for (VI).

H. W.

**Reactions of morpholine.** A. R. Ingram and W. F. Luder (*J. Amer. Chem. Soc.*, 1942, **64**, 2506—2507).—Morpholine and SnCl<sub>4</sub> give a 2:1 additive compound, m.p. 215—235° (decomp.). In hot CCl<sub>4</sub> or CHCl<sub>3</sub> rapidly, or slowly in the cold, it gives the hydrochloride and (?) 1-tri- or 1-di-chloromethylmorpholine, respectively.

R. S. C.

**Amino-ketones. I. Synthesis of amino-alcohols and  $\alpha$ -diamino-compounds from  $\beta$ -amino-ketones.** N. H. Cromwell, Q. T. Wiles, and O. C. Schroeder (*J. Amer. Chem. Soc.*, 1942, **64**, 2432—2435).—CHPh·CH·COMe with morpholine or piperidine in light petroleum (b.p. 88—100°) at the b.p. and then 0° and finally with HCl gives  $\delta$ -morpholino- (I), m.p. 152°, and  $\delta$ -piperidino- $\delta$ -phenylbutan- $\beta$ -one-hydrochloride (II), m.p. 158°, converted by KOH—NH<sub>2</sub>OH, HCl—MeOH—H<sub>2</sub>O at room temp. into  $\alpha$ -morpholino-, m.p. 107°, and  $\alpha$ -piperidino- $\gamma$ -oximino- $\alpha$ -phenylbutane, m.p. 105°, respectively, which with H<sub>2</sub>—Raney Ni—EtOH give the base and Ph·[CH<sub>2</sub>]<sub>2</sub>·CHMe·NH<sub>2</sub> but with Na—EtOH give  $\gamma$ -amino- $\alpha$ -morpholino-, b.p. 130°/1 mm. (Bz derivative, m.p. 158°), and  $\alpha$ -piperidino- $\alpha$ -phenylbutane, b.p. 112°/1 mm. (Bz derivative, m.p. 144°), respectively. Catalytic hydrogenation of (I) or (II) causes fission, but 3% Na—Hg in H<sub>2</sub>O, kept just acid by HCl, at -3° yields  $\delta$ -morpholino- (hydrochloride, m.p. 156°; benzoate hydrochloride, m.p. 236°) and  $\delta$ -piperidino- $\delta$ -phenylbutan- $\beta$ -ol, b.p. 137°/1 mm. (hygroscopic hydrochloride; benzoate hydrochloride, m.p. 217°). Ph  $\beta$ -morpholino-, m.p. 178° (unchanged by Na—EtOH), and  $\beta$ -anilino- $\beta$ -phenylethyl ketoxime, m.p. 131°, are also prepared.

R. S. C.

**Benzylideneaminomorpholine compounds.** L. Dugan, jun., and H. M. Haendler (*J. Amer. Chem. Soc.*, 1942, **64**, 2502).—4-o-, m.p. 75—76.5°, -m-, m.p. 145—147.5°, and -p-hydroxybenzylidene-, m.p. 167—168°, 4-o-, m.p. 99—101°, and 4-m-nitrobenzylidene-, m.p. 114—114.5°, 4-vanillylidene-, m.p. 153—154.5°, and 4-piperonylideneaminomorpholine, m.p. 76—77°, 4-p-salicylidene-, m.p. 161—162°, -piperonylidene-, m.p. 167.5—169°, -vanillylidene-, m.p. 205—207°, -furfurylidene-, m.p. 208—209°, and 4-p- $\alpha$ -o'-hydroxyphenylethylideneaminophenylmorpholine, m.p. 206—207°, are described.

R. S. C.

**2-Phenyloxazole. *p*-Substituted derivatives.** J. J. Rosenbaum and W. E. Cass (*J. Amer. Chem. Soc.*, 1942, **64**, 2444—2445).—Et<sub>2</sub> *p*-nitrobenzylideaminoacetal, m.p. 56—57°, b.p. 165—168°/2 mm., or *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO·NH·CH<sub>2</sub>·CH(OEt)<sub>2</sub> with P<sub>2</sub>O<sub>5</sub>—H<sub>2</sub>SO<sub>4</sub> gives 2-*p*-nitrophenyloxazole (I) (40% and 45%, respectively), m.p. 163.5—164.5°, oxidised by KMnO<sub>4</sub> or aq. Br to *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO·NH<sub>2</sub> and reduced by H<sub>2</sub>—Raney Ni—EtOH or SnCl<sub>2</sub>—conc. HCl to 2-*p*-aminophenyloxazole, m.p. 121—123° [picrate, m.p. 182.5—184° (decomp.)]; Ac, m.p. 191.5—192.5°, Bz, m.p. 163.5—164.5°, *p*-NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>, m.p. 226.5—228°, and *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub> (II) derivative, m.p. 191.5—192.5°. Deamination yields 2-phenyloxazole, whence (I) is regenerated by KNO<sub>3</sub>—H<sub>2</sub>SO<sub>4</sub> at room temp. and later 70°. M.p. are corr. (II) is less effective than sulphathiazole in staphylococcal, or than sulphanilamide in streptococcal, infections in mice.

R. S. C.

**Taste differences in compounds having N·C(S)· linking.** C. Y. Hopkins (*Canad. J. Res.*, 1942, **20**, B, 268—273).—OH·CHMe·CH<sub>2</sub>·NH<sub>2</sub> (25 g.) and CS<sub>2</sub> (38 g.), refluxed with EtOH—KOH, yields 2-thion-5-methylthiazolidine, m.p. 72—73°; with 50 g. of CS<sub>2</sub>, the corresponding thiazolidine, m.p. 93—94°, is obtained in poor yield (cf. Gabriel and Ohle, A., 1917, i, 563). COMe·CHMeCl with KCNS in aq. NaHCO<sub>3</sub> at room temp. affords 2-keto-4:5-dimethylthiazoline, m.p. 149—150°, and with NH<sub>2</sub>·CS<sub>2</sub>·NH<sub>2</sub> in EtOH at room temp. 2-thion-4:5-dimethylthiazoline, m.p. 166—168°. Tcherniac's method (*J.C.S.*, 1919, **115**, 1071) applied to COMe·CH<sub>2</sub>Cl gives 2-keto-4-methylthiazoline, m.p. 193°. 5-Bromo-2-keto-4-methylthiazoline, m.p. 150°, was prepared by the method of Ochiai and Nagasawa (A., 1939, II, 455). OH·CMe<sub>2</sub>·CH<sub>2</sub>·NH<sub>2</sub> with CS<sub>2</sub>, refluxed in KOH—EtOH, yields 2-thion-4:4-dimethylthiazolidine, m.p. 123—125°. All m.p. corr. For taste differences in above and other compounds, see A., 1943, III, 236.

F. O. H.

**Reactions of retene- and phenanthra-quinoneimine with aldehydes. New example of an aldol-type condensation.** C. W. C. Stein and A. R.

Day (*J. Amer. Chem. Soc.*, 1942, **64**, 2567—2569).—Retenequinoneimine (**I**) with  $\text{Pr}^a\text{CHO}$  in presence of  $\text{NH}_2\text{Bu}^a$  or  $\text{NEt}_3$  in boiling abs. EtOH gives 84—92% of 2-*n*-propylreteneoxazole, m.p. 100.5—101.3°. Similarly, (**I**) and  $\text{PhCHO}$  in EtOH +  $\text{NH}_2\text{Bu}^a$  (68%),  $\text{NEt}_3$  (84%), or piperidine (92%) gives 2-phenylreteneoxazole (**II**), m.p. 174.5—176° (occasionally 178—180°), but use of  $\text{NH}_2\text{Ph}$  gives only 9.7% and of  $\text{C}_5\text{H}_5\text{N}$  or  $\text{NaOEt}$  gives none; use of  $\text{KOH-EtOH}$  gives ~25% of (**II**), much side-reaction occurring. *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ -(**I**)- $\text{NH}_2\text{Bu}^a$  in EtOH give 2-*o*-hydroxyphenylreteneoxazole (51%), m.p. 245.5—247°. Phenanthraquinoneimine with  $\text{PhCHO}$  and piperidine (97%),  $\text{NEt}_3$  (77%), or  $\text{NH}_2\text{Ph}$  (17.5%) in EtOH gives 2-phenylphenanthroxazole, m.p. 205—206°, or with  $\text{Pr}^a\text{CHO-NEt}_3\text{-EtOH}$  gives 2-*n*-propylphenanthroxazole (50%), m.p. 84—86°, neither condensation occurring in absence of base. The primary reaction is an aldol-type condensation thus ( $B = \text{base}$ ):  $\cdot\text{C}_{(9)}\text{O}\cdot\text{C}_{(10)}(\text{NH})\cdot + B \rightleftharpoons \text{BH}^+ + [\cdot\text{CO}\cdot\dot{\text{C}}\text{N}]^- \rightleftharpoons (+\text{RCHO}) [\cdot\text{CO}\cdot\dot{\text{C}}\text{N}\cdot\text{CHR}\cdot\text{O}]^- \rightleftharpoons (+\text{RCHO}) \cdot\text{CO}\cdot\dot{\text{C}}\text{N}\cdot\text{CHR}\cdot\text{OH} \rightleftharpoons \cdot\text{C}(\text{OH})\cdot\text{C}\cdot\text{N}\cdot\text{CR}\cdot\text{OH} \rightarrow (\text{II})$  etc. M.p. are corr. R. S. C.

**Reactions of retene- and phenanthra-quinoneimine with Schiff bases. New example of an aldol-type condensation.** C. W. C. Stein and A. R. Day (*J. Amer. Chem. Soc.*, 1942, **64**, 2569—2573).—Retenequinoneimine (**I**) with benzylidene-*n*-butylamine (**II**), b.p. 112—113°/4 mm., in boiling, dry EtOH gives 78% [93.5% if 2 mols. of (**II**) are used] of 2-phenylreteneoxazole (**III**). The reaction occurs also in  $\text{PhMe}$  and 1 mol. of  $\text{NH}_2\text{Bu}^a$  is evolved; (**II**) is not hydrolysed to  $\text{PhCHO}$ ; a reaction mechanism is discussed similar to that for the reaction with  $\text{RCHO-base}$  (preceding abstract) with  $\text{NR}$  replacing the second O, but it is uncertain whether loss of  $\text{NH}_2\text{R}$  occurs at or after ring-closure. The basicity of the Schiff's base or presence of a stronger base affects the yield: e.g.,  $\text{CHPh:NPh}$  and (**I**) give 21%, but in presence of piperidine (**IV**) (1 equiv.) give 90% of (**III**); with  $\text{CHPr}^a\text{:NBu}^a$ , (**I**) gives 7% of 2-*n*-propylreteneoxazole, but if (**IV**) is also added gives 23%;  $\text{CHPr}^a\text{:NPh}$  with or without (**IV**) gives no oxazole.  $\text{CHPr}^a\text{:NBu}^a$  is dimeric (Rast),  $\text{CHPh:NPh}$  and  $\text{CHPh:NBu}^a$  are mainly monomeric, but  $\text{CHPr}^a\text{:NBu}^a$  is trimeric; probably only the monomeric compound reacts. Phenanthraquinoneimine with (**II**) (79%),  $\text{CHPh:NPh}$  alone (21.7%) or with (**IV**) (85%) gives 2-phenylphenanthroxazole and with  $\text{CHPr}^a\text{:NBu}^a$  alone (0.8%) or with (**IV**) (30%) gives 2-*n*-propylphenanthroxazole but does not react with  $\text{CHPr}^a\text{:NPh}$ . R. S. C.

**Riboflavin monoborate, m.p. 290—292°, and tetrabenzoylriboflavin, m.p. 131—136°.**—See A., 1943, III, 189.

**Phenylthiolthiazolines.** J. B. Niederl and W. F. Hart (*J. Amer. Chem. Soc.*, 1942, **64**, 2487—2488).—Contrary to expectation (A., 1941, II, 206),  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NCS}$  with  $\text{PhSH}$ , *o*- and *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SH}$  (**I**), etc. gives 2-phenyl-, m.p. 171°, 2-*o*-tolyl-, m.p. 164°, and 2-*m*-tolyl- (**II**), m.p. 139°, -thiol-5-methylthiazoline, which are stable to acid and yield the corresponding picrates, m.p. 141°, 133°, and 118°, respectively. With aq.  $\text{NaHCO}_3$ , (**II**) gives (**I**) and 5-methylthiazolid-2-one, keto-, m.p. 39°, and enol (hydrochloride, m.p. 204°) form.

R. S. C.

**Properties of the nitrogen-carbon nitrogen system in  $N^1$ -heterocyclic sulphanilamides.** R. G. Shepherd, A. C. Bratton, and K. C. Blanchard (*J. Amer. Chem. Soc.*, 1942, **64**, 2532—2537).—Contrary to statements in the literature, notably Ewins *et al.* (B.P. 512,145, 517,272; B., 1940, 94, 326), sulphapyridine (**I**) and  $\text{CH}_2\text{N}_2\text{-Et}_2\text{O}$  give 50—80% of a 7:3 mixture of 2-sulphanilyl-*N*-methylaminopyridine, 2- $\text{X}\cdot\text{SO}_2\cdot\text{NMe}\cdot\text{C}_5\text{H}_4\text{N}$  (**II**), m.p. 86.5—87°, and 2-sulphanilylimido-1-methyl-1:2-dihydropyridine, 2- $\text{X}\cdot\text{SO}_2\cdot\text{N}\cdot\text{C}_5\text{H}_4\text{NMe}$  (**III**), m.p. 232—233°.  $N^4$ -Acetylsulphapyridine and  $\text{CH}_2\text{N}_2\text{-Et}_2\text{O}$  give more slowly a 6:4 mixture of 2- $N^4$ -acetylsulphanilyl-*N*-methylaminopyridine (**IV**), m.p. 119.5—120°, and 2- $N^4$ -acetylsulphanilylimido-1-methyl-1:2-dihydropyridine (**V**), m.p. 239—240°. The Na salt of (**I**) with  $\text{Me}_2\text{SO}_4$  or  $\text{CH}_2\text{PhCl}$  gives, as main products, (**III**) and 2-sulphanilylimido-1-benzyl-1:2-dihydropyridine (**VI**), m.p. 235°, respectively. The appropriate Na salt and halogen derivative yield similarly (**V**), 2- $N^4$ -acetylsulphanilylimido-1-carbethoxymethyl-, m.p. 212—213°, and -1-benzyl-1:2-dihydropyridine (**VII**), m.p. 213—214°, 2-sulphanilylimido-1-carbethoxymethyl-, m.p. 200.5—201° [and thence, by  $\text{KOH-MeOH}$ , the 1- $\text{CO}_2\text{H}\cdot\text{CH}_2$  derivative (**VIII**), +  $\text{H}_2\text{O}$ , m.p. 97—98°], and -1-carbamylmethyl-1:2-dihydropyridine (**IX**), m.p. 230° (decomp.) [with alkali gives (**VIII**)], 2-sulphanilylimido- (**X**), m.p. 250—251°, and 2- $N^4$ -acetylsulphanilylimido-3-methyl-2:3-dihydrothiazole (**XI**), m.p. 272—273°.  $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{Cl}$  and the appropriate Na salt at 130° give 2- $N^4$ -acetylsulphanilylimido-1- $\beta$ -hydroxyethyl-1:2-dihydropyridine, m.p. 217—218°, and -3- $\beta$ -hydroxyethyl-2:3-dihydrothiazole, m.p. 231—232° (decomp.), hydrolysed by  $\text{NaOH-EtOH}$  to 2-sulphanilylimido-1- $\beta$ -hydroxyethyl-1:2-dihydropyridine (**XII**), m.p. 184—185°, and -3- $\beta$ -hydroxyethyl-2:3-dihydrothiazole (**XIII**), m.p. 159—160°, respectively. Structures are proved by (i) alkaline hydrolysis of (**IV**) to (**II**), of (**V**) to (**III**), of (**VII**) to (**VI**), and of (**XI**) to (**X**), (ii) hydrolysis of (**II**)—(**XIII**) by 12*N*- $\text{HCl}$  at 100° to *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$  and the appropriate base, (iii) synthesis of (**IV**) from *p*- $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHMe}$  and 2-bromopyridine and of (**V**), (**VII**), and (**XI**) from *p*- $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$  and the appropriate *N*-substituted 1:2-dihydro-base, (iv) by conversion of the

$\text{CO}_2\text{Me}\cdot\text{CH}_2$  compound by  $\text{CH}_2\text{N}_2$  into an alkali-labile substance, and (v) spectroscopic evidence. In abs. EtOH 2-imino-1:2-dihydropyridines and -2:3-dihydrothiazoles show absorption max. at 3215 and 2600 Å., respectively. Absorption spectra show that (**I**), its Ac derivative and sulphathiazole contain large amounts of the imino-form in EtOH. 2-Aminothiazole and  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Et}$  at 130—180° give 2-imino-3-acetoxyethyl-, m.p. 153.5—154.5°, and thence 2-imino-3-hydroxyethyl-2:3-dihydrothiazole (picrate, m.p. 159.5—161°). The ring-Me and - $\text{OH}\cdot[\text{CH}_2]_2$  compounds are approx. as active biologically as the parent compounds *in vivo* (less *in vitro*), but the 2- $\text{XSO}_2\cdot\text{NMe}$ -compounds are almost inactive. M.p. are corr. R. S. C.

**Sulphanilamides of thiazoles etc.**—See B., 1943, III, 63.

**Chemotherapy of bacterial infections. VIII. Synthesis of carb-oxylic acid derivatives of 2-sulphanilamidothiazole.** K. Ganapathi, C. V. Deliwala, and M. V. Shirsat (*Proc. Indian Acad. Sci.*, 1942, **A**, 16, 126—128).—Addition of  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$  and  $\text{HCO}_2\text{Et}$  to Na in dry  $\text{Et}_2\text{O}$  and, after neutralisation, treatment of the product with  $\text{CS}(\text{NH}_2)_2$ , yields Et 2-aminothiazole-5-carboxylate, m.p. 160—161°. 2-Sulphanilamidothiazole derivatives are obtained by condensing the appropriate aminothiazole with *p*- $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$  in presence of  $\text{C}_5\text{H}_5\text{N}$ , hydrolysing the product with 5*N*- $\text{HCl-EtOH}$  (1:1) which may remove only Ac, and removal of the ester group by alkali. Protracted hydrolysis may cause decarboxylation. The following are described: Et 2-sulphanilamidothiazole-5-carboxylate, m.p. 227—228° (Ac derivative, m.p. 228—229°); 2-sulphanilamido-4-methylthiazole-5-carboxylic acid, m.p. 195°; Et 2-acetsulphanilamido-4-methylthiazole-5-carboxylate, m.p. 154° and 248° after resolidification; 2-sulphanilamidothiazole-4-acetic acid, m.p. 182° (Et ester, m.p. 170—171°); Et 2-sulphanilamido-4-methylthiazole-5-acetate, m.p. 183—184° (Ac derivative, m.p. 203—204°);  $\alpha$ -2-sulphanilamido-4-thiazolyl-hexoic acid, m.p. 157—158°, and “-tert.-” butyric acid, m.p. 174° (Et ester, m.p. 169—170°); 2-sulphanilamido-4-methyl-, m.p. 236—237°, and -4:5-dimethyl-, m.p. 243—244°, -thiazole. H. W.

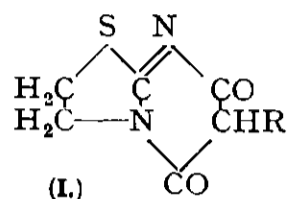
**Thiazoles. XXVI. Acyl derivatives of 2-aminothiazoles.** E. J. Masters and M. T. Bogert (*J. Amer. Chem. Soc.*, 1942, **64**, 2712—2713; see below).—2-Aminothiazole (**I**) with  $\text{CH}_2(\text{CO}_2\text{Et})_2$  and  $\text{NaOEt-EtOH}$  gives approx. equal amounts of Et *N*-2-thiazolylmalonamate (**II**), m.p. 149—149.5°, and malondi-2-thiazolylamide, darkens at ~258°, decomp. 271° [also obtained from (**II**) at > the m.p. or in boiling  $\text{NaOEt-EtOH}$ ].  $\text{CO}_2\text{K}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  gives similarly *N*-2-thiazolylmalonamic acid (54%), which at the m.p., 185.8—186.6°, gives  $\text{CO}_2$  and 2-acetamidothiazole, m.p. 206.5—207° (lit., 203°), also obtained from (**I**) by  $\text{Ac}_2\text{O}$ .  $\text{CHEt}(\text{CO}_2\text{Et})_2$  gives only (46%) Et *N*-2-thiazolylethylmalonamate [ $\alpha$ -carbethoxy-*n*-butyr-2-thiazolylamide], m.p. 117.8—118.8°. Cyclisation does not occur (cf. *loc. cit.*) as (**I**) cannot react as a 2- $\text{NH}\cdot$  compound. M.p. are corr. R. S. C.

**Reactions and derivatives of 2-aminobenzthiazole.** T. Wagner-Jauregg and E. Helmert (*Ber.*, 1942, **75**, [B], 935—949).—*o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  is converted by diazotisation and treatment with  $\text{CoCl}_2\cdot\text{KCNS}$  at 0—10° into *o*-nitrothiocyanobenzene, m.p. 136° (corr.), transformed by aq.  $\text{FeSO}_4\cdot\text{NH}_3$  at 100° into 2-aminobenzthiazole (**I**), m.p. 130—131° [hydrochloride, m.p. 238—240°; Et *H* sulphate, m.p. 130—132°, obtained from (**I**) and  $\text{Et}_2\text{SO}_4\cdot\text{H}_2\text{O}$  at room temp. and reconverted into (**I**) by dil. alkali hydroxide; Ac derivative (**II**), m.p. 189—192°]. 2-Hydnocarpamidobenzthiazole, m.p. 87—89°, obtained by use of the acid chloride in  $\text{C}_6\text{H}_6\text{-C}_5\text{H}_5\text{N}$ , is physiologically inactive. EtI and (**I**) give 2-amino-3-ethylbenzthiazoline, m.p. 83—87°. (**II**), EtI, and  $\text{NaOEt}$  in abs. EtOH at 100° followed by alkaline hydrolysis yield 2-ethyliminobenzthiazoline, b.p. 142°/0.14 mm., m.p. 88—89°. 2-Ethylimino-3-ethylbenzthiazoline has b.p. 125°/0.15 mm. (**I**) and  $\text{NEt}_2\cdot[\text{CH}_2]_2\cdot\text{Cl}\cdot\text{HCl}$  under  $\text{N}_2$  at 130—140° afford 2-imino-3- $\beta$ -diethylaminoethylbenzthiazoline, b.p. 165—175°/0.2 mm. [dihydrochloride, m.p. 263—265° (decomp.)]. Similarly, 2-amino-6-ethoxybenzthiazole (**II**) gives 2-imino-6-ethoxy-3- $\beta$ -diethylaminoethylbenzthiazoline, b.p. 190—205°/0.4 mm. [dihydrochloride, m.p. 241—242° (decomp.)]. When heated with  $\text{NEt}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ , quartz sand, and  $\text{P}_2\text{O}_5$  at 200° (**I**) yields a fraction, b.p. 160—180°/0.2 mm., and a compound,  $\text{C}_{20}\text{H}_{22}\text{N}_4\text{S}_2$ , possibly  $\text{S}\langle\text{C}_6\text{H}_4\rangle\text{N}\cdot[\text{CH}_2]_2\cdot\text{NEt}\cdot\text{C}\langle\text{S}\rangle\text{C}_6\text{H}_4$ , m.p. 88—89° (sulphate, m.p. 230—233°, softens at 205° and shrinks together at 210° when slowly heated; ethiodide, m.p. 224°). Freshly distilled  $\text{MeCHO}$  and (**I**) in  $\text{C}_6\text{H}_6$  yield 2-imino-3- $\alpha$ -hydroxyethylbenzthiazoline, m.p. 120—122° when rapidly heated, which with  $\text{P}_2\text{O}_5$  and (**I**) in  $\text{C}_6\text{H}_6$  at room temp. gives di- $\alpha$ -2-imino-3-benzthiazolinylethane, m.p. 165—167°. (**I**) when heated at 230° under  $\text{N}_2$ , preferably in presence of  $\text{Pd-C}$  or with quartz- $\text{P}_2\text{O}_5\cdot\text{H}_2\text{O}$  at 200°, affords 2-imino-3-benzthiazolyl-2'-benzthiazoline, m.p. 257—258° (Ag and Na, m.p. >360°, salts). (**II**) is transformed by  $\text{NH}_4\text{Cl}$  at 230—250° into 2-imino-6-ethoxy-3-6'-ethoxy-2-benzthiazolylbenzthiazoline, m.p. 217—219°. 2-Acetamidobenzthiazole is oxidised by  $\text{H}_2\text{O}_2$  in AcOH at 100° to 1-keto-2-acetamidobenzthiazole, m.p. 196°, hydrolysed by  $\text{HCl}$  (d 1.19)-aq.  $\text{Pr}^a\text{OH}$  at 100° to 1-keto-2-aminobenzthiazole hydrochloride, decomp. 225°, darkens at 220°. 1-Keto-2-imino-3-ethylbenzthiazoline,

m.p. 211—213°, is obtained similarly. Diazotised arsanilic acid and (I) yield the compound,  $C_{13}H_{11}O_3N_4SAs$ , m.p. 176—178° ( $C_5H_5N$  salt). H. W.

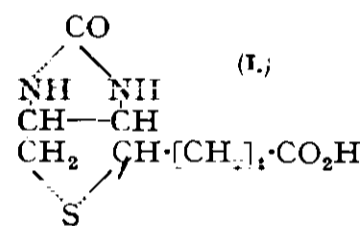
**Benzthiazoles.**—See B., 1943, II, 75.

**Thiazoles. XXV. Thiazolidinopyrimidines of barbituric acid type.** E. J. Masters and M. T. Bogert (*J. Amer. Chem. Soc.*, 1942, 64, 2709—2712; cf. A., 1942, II, 153).—Adding  $(CH_2)_2NH$  to 48% HBr at 0—5° (not the reverse addition) gives  $Br\cdot[CH_2]_2\cdot NH_2\cdot HBr$  (80%), new m.p. 172.3—174.3°, and thence (KCNO)  $Br\cdot[CH_2]_2\cdot NH\cdot CS\cdot NH_2$  (60%), new m.p. 173.6—174.2°, and (aq NaOH) 2-aminothiazoline (86%), m.p. 84—85°, which, reacting as the 2-NH<sub>2</sub> compound, with  $CH_2(CO_2Et)_2$  in boiling NaOEt-EtOH (not alone at 195°) gives 4:6-diketo-1:4:5:6-tetrahydrothiazolidino-3':2'-1:2-pyrimidine [ $5:7$ -dioxo-2:3:6:7-tetrahydro-5-thiazolo[3:2a]pyrimidine'] [(I), R = H] (88%), m.p. 244.5—245.5°. Use of  $CHR(CO_2Et)_2$  gives 4:6-diketo-5-methyl- (72%), m.p. 272—276°, -ethyl- (70%), m.p. 224.4—224.7°, -isopropyl- (76%), m.p. 262.3—262.8°, -phenyl- (45%), m.p. 247.2—247.7°, and -benzyl-1:4:5:6-tetrahydrothiazolidino-3':2'-1:2-pyrimidine [(I), R = Alk etc.] (82%), m.p. 241.9—242.3°.



NaOEt-AlkI-EtOH converts the substituted (I) into 4:6-diketo-5:5-diethyl- (29%), m.p. 138.2—138.7°, -5-ethyl-5-isopropyl- (33%), m.p. 92.6—93.1°, -5-ethyl-5-n-butyl- (31%), m.p. 89.7—90.3°, -5-phenyl-5-ethyl- (36%), m.p. 120.3—121.3°, and -5-benzyl-5-ethyl-1:4:5:6-tetrahydrothiazolidino-3':2'-1:2-pyrimidine (30%), m.p. 136—136.4°. With *iso*- $C_5H_{11}O\cdot NO$  in 30% EtOH at room temp.—50°, [(I), R = H] gives the 6-N-OH-compound (61%), m.p. 175—178°, converted by  $Na_2S_2O_4\cdot NH_3\cdot H_2O$  into the 6-NH<sub>2</sub>-compound (54%). + $H_2O$ , red at 174°, decomp. 194°. KCNO in hot  $H_2O$  then gives the 6-carbamido-derivative (80%), m.p. 261—263°, which with  $H_2C_2O_4$  at 185° gives thiazolidino-2':3'-2:3- or -3':2'-1:2-uric acid (36%), m.p. >300°. M.p. are corr. R. S. C.

**Structure of biotin: dethiobiotin.** V. du Vigneaud and D. B. Melville (with K. Folkers, D. E. Wolf, R. Mazingo, J. C. Keresztesy, and S. A. Harris) (*J. Biol. Chem.*, 1943, 146, 475—485; cf. A., 1942, II, 387).—Biotin (I) is converted into its Me ester, which with Raney



Ni in boiling 90% EtOH gives dethiobiotin Me ester [*Me* ε:5-(4-methylglyoxalid-2-one)hexoate] (II), m.p. 69—70°,  $[α]_D^{25} + 2.6°$  in  $CHCl_3$ , converted by HCl at 200° in a sealed tube into the dethiodiaminocarboxylic acid dihydrochloride (ζ-diaminononoic acid dihydrochloride), m.p. 180—182°,  $[α]_D^{25} + 4.04°$  in MeOH. The corresponding sulphate (III), m.p. 242—243°,  $[α]_D^{25} + 7.75°$  in  $H_2O$ , is obtained from (II) and aq.  $Ba(OH)_2$  at 140°, followed by  $H_2SO_4$ . (III) and  $HIO_4$ -aq. NaOH at room temp. (12 hr.), then at 40° (3 hr.) and 75° (2.5 hr.), give a product, which after sublimation in high vac. yields pimelic acid and a trace of adipic acid. Et ε-bromohexoate and  $CH_3AcNa\cdot CO_2Et$  give, after hydrolysis of the Et ester, b.p. 144—148°/0.9 mm., η-ketononoic acid, m.p. 39—40°, b.p. 135°/0.9 mm.; its Et ester, b.p. 91—96°/0.4 mm., with  $EtO\cdot NO\cdot HCl\cdot EtOH$  at 50°, followed by  $NH_2OH\cdot HCl\cdot NaOAc$ , affords Et ζ-dioximinononoate, m.p. 107—108°, hydrogenated (Raney Ni at 50—55°/140 atm.; liquid  $NH_3\cdot MeOH$ ) to Et ζ-diaminononoate [sulphate, m.p. 274° (decomp.)]. Phenanthrenequinone (IV) in EtOH converts the latter into Et 2-methyldibenzoquinoxaline-3-hexoate, m.p. 78—79°; the free acid, m.p. 186—187°, obtained by alkaline hydrolysis of the ester, is also obtained when (III) is converted into the free acid with  $Ba(OH)_2$ , followed by reaction with (IV). A. T. P.

**Structure of biotin: formation of thiophenvaleric acid from biotin.** D. B. Melville, A. W. Moyer, K. Hofmann, and V. du Vigneaud (*J. Biol. Chem.*, 1943, 146, 487—492).—The structure of biotin as 2'-keto-3:4-glyoxalido-2-tetrahydrothiophenvaleric acid is confirmed. The diaminocarboxylic acid sulphate from biotin and  $Me_2SO_4$ -aq. KOH, followed by refluxing the acidified (HCl) mixture, give δ-2-thienylvaleric acid, m.p. 40—41°, identical with that obtained by reducing γ-2-thienoylbutyric acid (I), m.p. 92—94°, with Zn-HCl. (I) is prepared from glutaric anhydride and thiophen (Friedel-Crafts) and is oxidised by alkaline  $KMnO_4$  to thiophen-2-carboxylic acid. A. T. P.

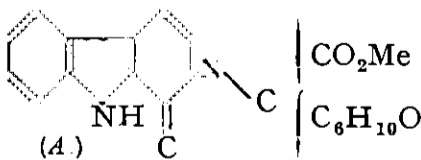
**Coccarboxylase and related esters.** J. Weijlard (*J. Amer. Chem. Soc.*, 1942, 64, 2279—2282).—Aneurin hydrochloride with  $H_4P_2O_7\cdot Na_4P_2O_7$  at 150—155° gives the orthophosphate ester,  $RH_2PO_4$ , + $2H_2O$ , m.p. 200—202°, with conc.  $H_2SO_4$  at 150° give the H sulphate ester,  $RHSO_4$ , + $H_2O$ , m.p. 258—259° (decomp.), and with  $HPO_3$  or  $H_4P_2O_7\cdot P_2O_5\cdot Na_4P_2O_7\cdot NaPO_2$  at ~150° gives the pyrophosphate (coccarboxylase) (I), (~10%), +0.75—1 $H_2O$ , m.p. 238—240°. 4-Methyl-5-hydroxyethylthiazole with  $H_4P_2O_7$  at 150—160° gives the orthophosphate ester, + $H_2O$ , m.p. 162°, but with  $HPO_2$  at 150—155° gives the pyrophosphate ester (Ag salt,  $RAg_3P_2O_7$ , +0.6 $HNO_3$ , +3 $H_2O$ ), which with 4-amino-2-methyl-5-bromo-

methylpyrimidine hydrobromide (II) in liquid paraffin at 110° gives (I) (10%), which is also obtained (10%) from 4-methyl-5-β-chloroethylthiazole, (II), and  $Ag_4P_2O_7$  in liquid paraffin at 110°. R. S. C.

## VII.—ALKALOIDS.

**Formation of nicotine in plants grafted on tobacco.**—See A., 1943, III, 292.

**Alstonia alkaloids. I. Degradation of alstonine to β-carboline bases and the reduction of tetrahydroalstonine with sodium and butyl alcohol.** N. J. Leonard and R. C. Elderfield (*J. Org. Chem.*, 1942, 7, 556—572; cf. Sharp, A., 1934, 538, 1117; 1938, II, 463).—The composition,  $C_{21}H_{20}O_3N_2$ , is confirmed for alstonine (I) from *A. constricta*, F. Muell, by analyses of the sulphate dihydrate, m.p. 195—196°, decomp. 208°,  $[α]_D^{25} + 127° \pm 2°$  in  $H_2O$ , sulphate tetrahydrate, m.p. 203—204°,  $[α]_D^{25} + 120° \pm 2°$  in  $H_2O$ , H sulphate, m.p. 243—244° (decomp.),  $[α]_D^{25} + 120° \pm 2°$  in  $H_2O$ , platinichloride, m.p. 220—221° (decomp.), hydrochloride, m.p. 278—279° (decomp.),  $[α]_D^{25} + 141° \pm 2°$  in  $H_2O$ , nitrate, m.p. 252—254° (decomp.), hydriodide, m.p. 270° (decomp.), and perchlorate, m.p. 239—240°. (I) is hydrogenated ( $PtO_2$  but not Pd in abs. MeOH) to tetrahydroalstonine (II), m.p. 230—231°,  $[α]_D^{25} - 110° \pm 2°$  in  $CHCl_3$ ,  $[α]_D^{27} - 88° \pm 2°$  in  $C_6H_5N$ , which is not formed by attempted reduction of salts of (I) or (I) in AcOH in presence of  $PtO_2$ . (II) gives a colour similar to that of yohimbine in the Adamkiewicz test. Fusion of (I) with KOH gives harman (III), prisms or needles, m.p. 239—241° [further identified as the picrate, m.p. 257—258° (decomp.), aurichloride, m.p. 229.5—230° (decomp.), and  $CHPh$  derivative, m.p. 204—205°], but no volatile amine; a pure compound has not been isolated from the considerable basic fraction. Similar treatment of (II) affords (III), norharman, base A,  $C_{17}H_{16}N_2$ , m.p. 171.5—172.5° [picrate, m.p. >267° (decomp.)], which in  $HCl\cdot EtOH$  shows a marked blue fluorescence and is probably a β-substituted carboline, base B, considered tentatively to be  $C_{16}H_{16}N_2$  or  $C_{18}H_{18}N_2$  on the basis of analysis of its picrate, m.p. 261° (decomp.), which also gives a strong blue fluorescence, and base C, considered tentatively to be  $C_{17}H_{18}N_2$  on the basis of analysis of the picrate, m.p. 203.5—205.5° (decomp.). Indole-2-carboxylic acid is isolated from the acidic products of the fusion but a pure individual could not be isolated from the neutral fraction, which appears to contain indole derivatives. Thermal decomp. of (I) yields a series of bases all apparently derived from β-carboline although none has been definitely identified. These are base D,  $C_{17}H_{18}N_2$ , readily isolated by taking advantage of the very sparing solubility of its picrate, m.p. 254—256°, in EtOH, which appears to be isomeric with base C; base E,  $C_{18}H_{20}N_2$  or  $C_{19}H_{22}N_2$  (picrate, m.p. 193.5—195°), not identical with Sharp's alstyrine, and base F,  $C_{13}H_{12}N_2$ , m.p. 79—81° [picrate, m.p. 261—262.5° (decomp.)]; hydrochloride, m.p. ~275° (decomp.), becomes brown at 227°; methiodide, m.p. 283—284° (decomp.). The ultra-violet absorption spectrum of F closely resembles that of 2-ethyl-β-carboline (IV). γ-Aminobutaldehyde  $Et_2$  acetal,  $NPhEt\cdot NH_2$ , and fused  $ZnCl_2$  afford 1-ethyltryptamine, b.p. 170—171°/2 mm. (phthalimide, m.p. 149—150°; picrate, m.p. 178.5—180.5°), converted by dil.  $H_2SO_4$  and 40%  $CH_2O$  at 70° and subsequently by boiling dil.  $H_2SO_4$  into 1-ethyl-2:3:4:5-tetrahydro-β-carboline, isolated as the picrate, m.p. 224—225°, and p- $NO_2\cdot C_6H_4\cdot CO$  derivative, m.p. 146—148°; the base is dehydrogenated by Pd-black at 160—170° to (IV), m.p. 41—42° (picrate, m.p. 227—228°; methiodide, m.p. 293—295°), not identical with F. Norharman ethiodide, m.p. 198—199°, is treated with an excess of NaOH and the ppt. is dried over  $P_2O_5$  at room temp. and then at 100°, after which it is repeatedly treated with evaporating PhMe, thus giving 3-ethyl-β-isocarboline, m.p. 176.5—178.5° [ethiodide, m.p. 213.5—215°, also prepared from (IV)], which is not identical with F. 2-Ethyl-β-carboline, m.p. 193—195°, is obtained by treating tryptophan with  $EtCHO$  in dil.  $H_2SO_4$  and oxidising the product with  $K_2Cr_2O_7$ . The product obtained by the distillation of (I) with Zn dust appears identical with F. (II) is reduced by Na in boiling BuOH to hexahydroalstanol, m.p. 282—284° (decomp.),  $[α]_D^{27} - 78° \pm 3°$  in  $C_6H_5N$  [picrate, m.p. 237—238° (decomp.)]; acetate, m.p. 95—96°, and its picrate, m.p. 223—224.5° (decomp.).  $CO_2Me$  of (II) is reduced to  $CH_2\cdot OH$  and 2 H are added but the exact relationship of initial and final substances is not clear. The ultra-violet absorption suggests that the compound is an αβ-disubstituted

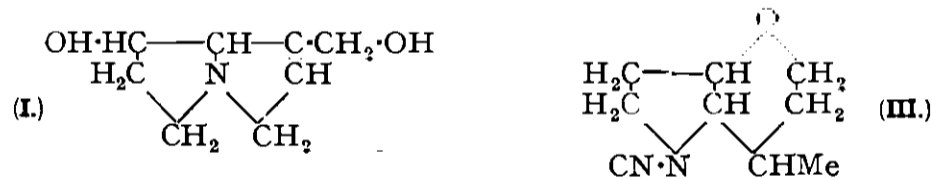


indole. The formula for (I) may be partly resolved as in (A). (I) is inactive in doses of 35 mg. per day in birds infected with avian malaria. M.p. are corr. H. W.

**Alstonia alkaloids. II. New alkaloid, alstoniline, from A. constricta.** W. L. Hawkins and R. C. Elderfield (*J. Org. Chem.*, 1942, 7, 573—580).—The isolation is described of alstoniline (I), decomp. 372°, a minor alkaloid of *A. constricta* in which it occurs to the extent of 0.02—0.05% of the bark. It exists also as the cryst. monohydrate (II),  $C_{22}H_{18}O_3N_2\cdot H_2O$ , decomp. 356°. Derivatives of (I) fall into two groups depending on whether or not this  $H_2O$  is present. (II) is obtained by neutralising the hydrochloride (III)

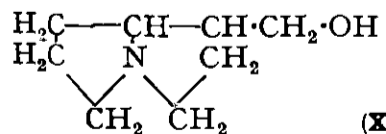
which contains 1 H<sub>2</sub>O and decomposes over a wide range when heated without melting, whereas (I) is derived by neutralising the anhyd. sulphate (IV), m.p. 260—264° (decomp.). All derivatives of (II) (e.g. the picrate, decomp. 294°) retain 1 H<sub>2</sub>O whereas compounds derived from (I) may or may not be anhyd. (e.g., anhyd. picrate, explosive decomp. >350°; anhyd. methiodide, decomp. without melting over a wide temp. range). (I) is transformed into (II) by crystallisation from 95% EtOH. The similarity between the ultra-violet absorption curves of (I) and (II) indicates that hydration does not involve a basic change in the arrangement of the double linking of the two substances. Aeration of a solution of (II) in EtOH for several hr. gives a cryst. product, C<sub>22</sub>H<sub>18</sub>O<sub>4</sub>N<sub>2</sub>·H<sub>2</sub>O, m.p. 212—213°, provisionally named *alstoniline oxide* (V). Reduction (PtO<sub>2</sub>) of (II) leads to the absorption of 2 H<sub>2</sub>, the colour of the solution changing from dark orange-red to a strongly fluorescent yellow. On exposure to air in the working up of the product, the absorbed 2 H<sub>2</sub> is removed and 1 O is absorbed with production of (V). Attempts to isolate the reduced base by crystallisation under N<sub>2</sub> were fruitless. Similar reduction of (III) gives a H<sub>4</sub>-salt, m.p. 231—232° (decomp.), and of (IV) gives a H<sub>8</sub>-compound (VI), m.p. 233—234° (decomp.). These salts are stable to air. In one instance an attempt to form a methiodide of (II) by heating (II) with a large excess of Mel in C<sub>6</sub>H<sub>6</sub> at 70° for several hr. led to a second form of (II), m.p. 189—190°. This is unstable, being oxidised when solid or in solution, by air to (V). All derivatives of (I) are optically inactive. (II) gives a negative result with Ehrlich's reagent. The colour changes of (VI) in the Adamkiewicz reaction as modified by Harvey *et al.* are similar to those observed with tetrahydroalstonine and indicate the probable presence of a tetrahydro-β-carboline ring system. (II) gives an entirely different colour series with this reagent. The presence of 2 OMe in (V) is indicated by analysis. *A. constricta* and several of its alkaloid fractions have been found to be inactive in avian malaria. M.p. are corr. H. W.

**Structure of monocrotaline. VII. Structure of retronecine and related bases.** R. Adams, M. Carmack, and J. E. Mahan. **VIII. Proof of primary and sec. hydroxyl groups in retronecine.** R. Adams and K. E. Hamlin, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2593—2597, 2597—2599; cf. A., 1941, II, 154).—VII. Relative basic strengths of retronecine (I) and its derivatives and chemical reactions indicate the annexed structure. Retronecanol (II) and CNBr in Et<sub>2</sub>O give an oily additive compound, which, when kept at 2° or better (28%)



boiled in C<sub>6</sub>H<sub>5</sub>N, give the 1'-CN-derivative (III), m.p. 94.5—95° (corr.), hydrolysed by hot 15% H<sub>2</sub>SO<sub>4</sub> to 4-methyl-2:3:5:6-tetrahydropyrrolidino-3':2'-2:3-pyran, an oil [*picrate*, m.p. 121.5—122.5° (corr.)], which with CNBr regenerates (III) and with Mel-COMe<sub>2</sub> gives 4:1'-dimethyl-2:3:5:6-tetrahydropyrrolidino-3':2'-2:3-pyran hydrobromide, m.p. 195—196° (corr.). The following pK<sub>H</sub> are recorded (cf. A., 1943, II, 102): (I) 8.94, platynecine (IV) 10.22, deoxyretronecine (V) 9.55, retronecanol (VI) 10.91, anhydro-platynecine (VII) 9.42, heliotridane (VIII) 11.48, heliotridene (IX) 10.60, and isoretronecanol (X) (see below) 10.88. In accordance with (I) etc., Kuhn-Roth determinations show no CMe in (I), (IV), (VII), or (X) and 0.40—0.69 CMe in (V), (VI), (VIII), and (IX).

VIII. The presence of primary and sec. OH in (I) is proved. Platynecine benzoate, new m.p. 118—119°, [α]<sub>D</sub><sup>25</sup> -88.6°, gives the Cl-compound, m.p. 72—73°, [α]<sub>D</sub><sup>25</sup> -14.5° (cf. A., 1936, 1277), which with H<sub>2</sub>-Raney Ni in EtOH at 2—3 atm. gives isoretronecanol benzoate (86%), m.p. 56—57°, b.p. 161.5—162.5°/1.2 mm., [α]<sub>D</sub><sup>28</sup> -60.8° (hydrochloride, m.p. 181—182°, [α]<sub>D</sub><sup>28</sup> -48.6°), and thence (aq. NaOH) (X) [= 1-hydroxymethylpyrrolizidine] (74%), m.p. 39—40°, b.p. 115—116°/1—2 mm., [α]<sub>D</sub><sup>27</sup> -78.2° [methiodide, m.p. 281—282° (decomp.)]; *picrate*, m.p. 194—195° (decomp.)]. With CrO<sub>3</sub>-AcOH,

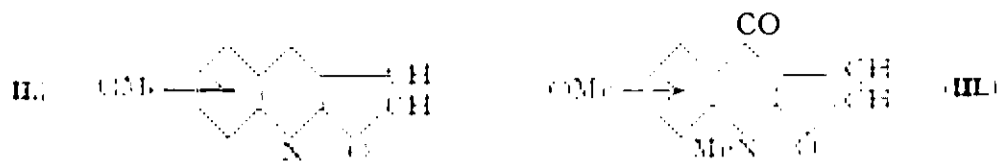


added gradually, this gives 1-carboxypyrrolizidine, m.p. 228—229° (decomp.), [α]<sub>D</sub><sup>28</sup> -65.8° [*picrate*, m.p. 220—221° (decomp.)], which with CH<sub>2</sub>N<sub>2</sub> gives the Me betaine [*chloroaurate*, m.p. 224—225° (decomp.)]; *picrate*, m.p. 194—195° (decomp.)]. Al(OBu<sup>n</sup>)<sub>3</sub>-cyclohexanone-PhMe at the b.p. oxidises (II) to retronecanone (30%), unstable, b.p. 95—96°/15 mm., [α]<sub>D</sub><sup>30</sup> -96.7° [*picrate*, m.p. 195° (decomp.)]; *semicarbazone*, m.p. 209—210° (decomp.); *oxime*, m.p. 167—168°, [α]<sub>D</sub><sup>28</sup> -76.0°. M.p. are corr. [α] are in EtOH.

R. S. C.

**Argentine plants. V. Identification and characterisation of alkaloids in *Fagara coco* (Gill), Engl.** V. Deulofeu, R. Labriola, and F. De Langhe (*J. Amer. Chem. Soc.*, 1942, **64**, 2326—2328; cf. A., 1942, II, 275).—Leaves and twigs (10 kg.) of this plant yield skimmianine (previously called β-fagarine) (13 g.), α- (I), (OMe)<sub>2</sub>C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>·NMe (7 g.), dimorphic, m.p. 163° and 169°, [α] 0,

and γ-fagarine (II), C<sub>13</sub>H<sub>11</sub>O<sub>3</sub>N (6 g.), m.p. 142° (*picrate*, m.p. 177°; *picrolonate*, m.p. 174—175°). The structure of (II) is as shown, for with Mel at 100—105° it gives iso-γ-fagarine (III), m.p.



179°, and with KMnO<sub>4</sub> in hot COMe<sub>2</sub> gives γ-fagaraldehyde [2-hydroxy-4:α-dimethoxyquinoline-3-aldehyde], m.p. 185° (*phenylhydrazone*, m.p. 207°), and thence (KMnO<sub>4</sub>-COMe<sub>2</sub>) γ-fagaric acid, m.p. 215° [also obtained similarly from (II)], which in boiling dil. HCl yields 2:4-dihydroxy-α-methoxyquinoline, m.p. 250° [NO-derivative, m.p. 216—217° (decomp.)]. (I) differs in behaviour and structure. R. S. C.

## VIII.—ORGANO-METALLIC COMPOUNDS.

**Composition of magnesium alkyl chloride solutions in ethyl ether.** C. R. Noller and A. J. Castro (*J. Amer. Chem. Soc.*, 1942, **64**, 2509—2510).—Previous views (A., 1940, II, 300) are incorrect, since distribution of the Cl in MgBu<sup>n</sup>Cl-Et<sub>2</sub>O depends on access of traces of H<sub>2</sub>O. R. S. C.

**Condensations by sodium. XXI. Sodium *n*-octyl and *n*-decyl.** A. A. Morton, J. B. Davidson, and R. J. Best. **XXII. General theory of the Wurtz reaction. The initial step.** A. A. Morton, J. B. Davidson, and H. A. Newey. **XXIII. General theory of the Wurtz reaction. II. Second phase.** A. A. Morton, J. B. Davidson, and B. L. Hakan. **XXIV. Pyrolysis of sodium amyl.** A. A. Morton and H. A. Newey. **XXV. Reactions of sodium amyl with naphthalene, acenaphthene, and decahydronaphthalene.** A. A. Morton, J. B. Davidson, T. R. P. Gibb, jun., E. L. Little, E. F. Clarke, and A. G. Green (*J. Amer. Chem. Soc.*, 1942, **64**, 2239—2240, 2240—2242, 2242—2247, 2247—2250, 2250—2253; cf. A., 1941, II, 123).—XXI. NaC<sub>8</sub>H<sub>17</sub>-*n* and NaC<sub>10</sub>H<sub>21</sub>-*n* resemble NaC<sub>5</sub>H<sub>11</sub>. Bubbling CO<sub>2</sub> into *n*-C<sub>8</sub>H<sub>17</sub>Cl (I) and Na in light petroleum at -10° gives *n*-C<sub>8</sub>H<sub>17</sub>·CO<sub>2</sub>H (49%), *n*-C<sub>7</sub>H<sub>15</sub>·CH(CO<sub>2</sub>H)<sub>2</sub> (15%), and *n*-C<sub>10</sub>H<sub>19</sub> (7%); yields are 23, 26, and 6%, respectively, if CO<sub>2</sub> is passed over the surface; the supernatant solution alone gives no acid. With PhMe and Na at 72°, (I) gives 51% of *n*-C<sub>8</sub>H<sub>17</sub>Ph, but with C<sub>6</sub>H<sub>6</sub> gives only C<sub>8</sub>H<sub>18</sub> (68%), BzOH (33%), and traces of CPh<sub>3</sub>·OH and (?) *n*-C<sub>8</sub>H<sub>17</sub>Ph, and with PhOMe gives a little PhOH and acid. *n*-C<sub>10</sub>H<sub>21</sub>Cl with Na and CO<sub>2</sub> or PhMe gives similarly *n*-C<sub>10</sub>H<sub>21</sub>·CO<sub>2</sub>H (28.4%) + *n*-C<sub>9</sub>H<sub>19</sub>·CH(CO<sub>2</sub>H)<sub>2</sub> (2.3%) or *n*-undecylbenzene (74%), b.p. 296°±1° (*p*-sulphonamide, m.p. 95.7—96.2°), respectively.

XXII. It is not necessary to assume existence of free radicals for formation of NaAlk compounds. The yield of NaC<sub>8</sub>H<sub>17</sub>-*n* from Na (1 atom) and *n*-C<sub>8</sub>H<sub>17</sub>Cl (1 mol.) in *n*-C<sub>8</sub>H<sub>18</sub> is raised to 72% by very rapid stirring. Primary AlkCl and Na produce insol., jelly-like coatings, readily penetrated by AlkCl and removed or burst by newly formed NaAlk; *sec*.-AlkCl give solid, impenetrable coatings which prevent further reaction. AlkCl give good yields of NaAlk as the halide can penetrate the coating of NaAlk without reacting with it; such reaction deposits NaCl which stops further formation of NaAlk. Thus, high yields of NaAlk depend on presence of an excess of finely divided Na, absence of a protective coating on it, and an unreactive C-halogen linking. The assumption that the Na acts as a trap for alkyl radicals is negated by the relatively large size of the Na particles and by the fact that the yield of NaC<sub>8</sub>H<sub>17</sub>-*n* is the same whether C<sub>8</sub>H<sub>17</sub>Cl is added to Na or vice versa. Interaction of activated Na with Bu<sup>n</sup>Cl in light petroleum at 18—20° and pouring the mixture on to CO<sub>2</sub> gives 42.2% of Bu<sup>n</sup>CO<sub>2</sub>H and 3.3% of CHPr<sup>n</sup>(CO<sub>2</sub>H)<sub>2</sub>.

XXIII. Free radicals have no part in the second phase (NaAlk + AlkHal → Alk<sub>2</sub>) of the Wurtz reaction. When the alkyl chains of NaCH<sub>2</sub>R and R'·[CH<sub>2</sub>]<sub>2</sub>·Hal are sterically adjacent during interaction, prototropic change leads to RMe and CHR'·CH<sub>2</sub>; this distribution of paraffin and olefine predominates in the products from NaC<sub>8</sub>H<sub>17</sub>-EtHal and -PrHal, NaC<sub>5</sub>H<sub>11</sub>-AlkHal (12 examples), NaC<sub>6</sub>H<sub>13</sub>-C<sub>5</sub>H<sub>11</sub>Cl and -C<sub>8</sub>H<sub>17</sub>Cl. The relative amounts are, however, somewhat obscured by the change, NaAlk + Alk'Hal → NaAlk' + AlkHal, which occurs most readily with iodides and least readily with chlorides. When this change occurs readily, the yield of symmetrical Alk<sub>2</sub> should be high; this is so for interaction of NaC<sub>5</sub>H<sub>11</sub> with AlkHal. Free radicals, if formed, should give the same relative amounts of products independently of their source; this is not the case for NaC<sub>8</sub>H<sub>17</sub> with MeCl, MeBr, or Mel. Reputed analogies requiring free radical mechanisms are false analogies.

XXIV. Heating NaC<sub>5</sub>H<sub>11</sub> at 110—120° before interaction with CO<sub>2</sub> reduces the amount of *n*-C<sub>5</sub>H<sub>11</sub>·CO<sub>2</sub>H formed, a large fall in yield occurring at 80—90°; heating at 80—120° leads to some tarry acids; H<sub>2</sub>O-sol. acids are also formed (max. at 90—100°), containing >1 CO<sub>2</sub>H per C<sub>5</sub>-unit, the CO<sub>2</sub>H being attached to a remote C.

XXV. C<sub>10</sub>H<sub>8</sub> with NaC<sub>5</sub>H<sub>11</sub>-*n* or NaC<sub>8</sub>H<sub>17</sub>-*n* and then CO<sub>2</sub> in light petroleum at 72° (N<sub>2</sub>) gives α- + β-C<sub>10</sub>H<sub>7</sub>·CO<sub>2</sub>H (14, 17),

1:3- + 1:8- + 2:6- $C_{10}H_8(CO_2H)_2$  (10, 15), and  $C_{10}H_8(CO_2H)_3$  (2, 5%, respectively). Acenaphthene and  $NaC_5H_{11}-CO_2$  give the 1:5-dicarboxylic acid (~50%), m.p. 292—294° (Et<sub>2</sub> ester), converted by CaO-Cu-bronze at 280° into the 5- $CO_2H$ -compound and by  $KMnO_4$  at 50—60° into 1:4:8- $C_{10}H_8(CO_2H)_3$ . Decahydronaphthalene and  $NaC_5H_{11}-CO_2$  very readily give the (? 1:4:5:8-)( $CO_2H$ )<sub>4</sub>-compound, m.p. 61—62° (dianhydride, m.p. ~300°); impure (?) amyl derivatives were obtained by alkylation. R. S. C.

## IX.—PROTEINS.

**Electrophoretic study of the proteins in rubber latex serum.** C. P. Roe and R. H. Ewart (*J. Amer. Chem. Soc.*, 1942, **64**, 2628—2632).—Serum from unpreserved rubber latex (from Florida or Sumatra) contains seven electrophoretically distinct proteins, for five of which the relation between electrophoretic mobility and pH is determined. Preservation by  $NH_3$  rapidly alters the proteins, reducing the separable components to two. Dry protein is obtained from rubber-free latex serum by sublimation in vac. without much alteration in electrophoretic properties. Modifications in procedure necessary for study of rubber latex are recorded. R. S. C.

**Catalysed hydrolysis of amide and peptide bonds in proteins.** J. Steinhardt and C. H. Fugitt (*J. Res. Nat. Bur. Stand.*, 1942, **29**, 315—327).—The rate of hydrolysis of amide and peptide linkings in wool and ovalbumin by strong acids of high mol. wt. is  $\gg$  by HCl, and the relative efficiencies of various acids as hydrolysing agents are in the same order as the affinities of their anions for the protein (cf. B., 1941, II, 338). Among compounds  $RO\cdot SO_3H$  where R = alkyl, those containing 14 C atoms show max. hydrolytic action. Addition of  $n-C_{12}H_{25}\cdot O\cdot SO_3Na$  (I) increases the hydrolytic breakdown produced by HCl, small amounts of the salt favouring decomp. of amide rather than peptide linkings. The effect of temp. on the rate of hydrolysis is decreased by addition of (I) to HCl. The mechanism of the catalysis and practical applications are discussed. C. S. W.

## X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

**New crystalline compounds of heparin.** D. A. Scott, A. F. Charles, and A. M. Fisher (*Trans. Roy. Soc. Canada*, 1942, [iii], **36**, V, 49—51).—Ba-heparin in  $H_2O$  with excess of piperidine, *iso*- $C_5H_{11}\cdot NH_2$ , and  $n-C_5H_{11}\cdot NH_2$  yields cryst. compounds which after drying over NaOH retain all the activity of the heparin (cat blood), and contain respectively 8.3, 6.1, and 6.8% of N. They undergo no apparent change when heated at 110° for 1 hr. Na- and  $NH_4$ -heparin yield similar compounds. No analyses are given. A. Li.

**Barbaloin.** L. N. Owen and J. L. Simonsen (*J. Amer. Chem. Soc.*, 1942, **64**, 2516—2517).—Hydrolysis of barbaloin (I) by borax does not give MeOH (Rosenthaler, *Pharm. Acta Helv.*, 1934, **9**, 9; Cahn *et al.*, A., 1932, 1252). The mol. wt. (521) of barbaloin Me ether, determined by X-ray analysis, establishes the formula,  $C_{21}H_{17}O_2(OMe)_7$ . (I) is thus the corresponding (OH)<sub>7</sub>-compound. R. S. C.

**Penillic acid, an optically active acid from penicillin.** W. M. Duffin and S. Smith (*Nature*, 1943, **151**, 251).—In aq. solution at pH 2, penicillin affords *penillic acid*, decomp. 175°, extracted with BuOH but not Et<sub>2</sub>O, and recryst. from  $H_2O$ . It shows a pale blue fluorescence in ultra-violet light, gives a deep bluish-purple colour with ninhydrin, possesses some of the properties of an  $NH_2$ -acid, but does not react to  $FeCl_3$  like penicillamine. A. A. E.

**Penicillamine, a characteristic degradation product of penicillin.** E. P. Abraham, E. Chain, W. Baker, and (Sir) R. Robinson (*Nature*, 1943, **151**, 107).—*Penicillamine*,  $C_6H_{11}O_4N\cdot HCl$  (but conceivably  $C_6H_9O_3N\cdot HCl\cdot H_2O$ ), is obtained by hydrolysing Ba penicillin at 100° for 1 hr. with 0.1N- $H_2SO_4$  and separating by means of  $HgCl_2$ . It is optically inactive. Three proton-binding centres at pH 2.0, 7.9, and 10.5, respectively, may be an acidic OH, the basic group, and a weakly acidic OH; N is present as  $NH_2$  and the substance gives an intense bluish-purple ninhydrin reaction. A typical  $\alpha$ - $NH_2$ -acid structure is improbable. Unusual behaviour (detailed) suggests relationship to an  $NH_2$ -sugar and ascorbic acid. A. A. E.

## XI.—ANALYSIS.

**Review of organic microchemistry.** L. T. Hallett (*Ind. Eng. Chem. [Anal.]*, 1942, **14**, 956—993).—The applications of micro-methods to the following are reviewed and discussed in detail: synthesis and purification of org. substances, including recrystallisation, sublimation, chromatographic separation, extractions; physi-

cal methods, including weighing and determination of consts.; the use of the microscope, and analysis for elements and sp. groups. Throughout stress is laid on special micro-apparatus, and many designs are given in detail. An extensive bibliography is appended. J. D. R.

**Identification of very small amounts of liquids.**—See A., 1943, I, 101.

**Preparation of "N/10-bromine."**—See A., 1943, I, 98.

**Semimicro-determination of chlorine, bromine, and iodine in organic compounds.** E. W. Peel, R. H. Clark, and E. C. Wagner (*Ind. Eng. Chem. [Anal.]*, 1943, **15**, 149—151).—The sample is fused in the Parr bomb with  $Na_2O_2$ ,  $KNO_3$ , and sucrose, lactose, or BzOH, and Cl determined gravimetrically as AgCl. If Br or I is to be determined  $BrO_3'$  or  $IO_3'$  is reduced with  $N_2H_4$  and determined as AgBr or AgI. Liquids are weighed into gelatin capsules for analysis. J. D. R.

**Micro-determination of sulphur and halogens by melting with potassium.**—See A., 1943, I, 98.

**Iodoform reaction by methods of microscopy.** H. F. Schaeffer (*J. Chem. Educ.*, 1942, **19**, 15—16).—The technique of carrying out the reaction on hanging drop and ordinary slides is described. L. S. T.

**Analytical data for the systems carbon tetrachloride-acetic acid-benzene and carbon tetrachloride-tetrachloroethylene.** W. R. McMillan and H. J. McDonald (*Ind. Eng. Chem. [Anal.]*, 1943, **15**, 114—116).—The ternary system  $C_6H_6-CCl_4-AcOH$  is analysed by titration of the AcOH with standard NaOH; during the titration the  $C_6H_6-CCl_4$  phase separates and is centrifuged and analysed by *n* determination. Alternatively the sample may be analysed by measurement of *d* and *n*. The binary system  $CCl_4-C_2H_2Cl_4$  is analysed by *n* determinations. J. D. R.

**Acetaldehyde determination in presence of formaldehyde and acetaldehyde by the polarographic method.** R. W. Mosher (*Ind. Eng. Chem. [Anal.]*, 1943, **15**, 107—109).— $CH_2=CH\cdot CHO$  is determined polarographically in presence of  $CH_2O$  and MeCHO in LiCl solution buffered to pH 7.0—8.0 with  $Li_3PO_4$ . During the determination the temp. must be held const. to  $\pm 0.05^\circ$ . J. D. R.

**Quantitative drop analysis. XVII. Gasometric determination of amino-nitrogen.** J. Sandkuhle, P. L. Kirk, and B. Cunningham (*J. Biol. Chem.*, 1943, **146**, 427—432; cf. A., 1941, II, 276).—A modification of the Van Slyke gasometric method for determination of  $\mu g.$  quantities of amino-N is described; 0.5  $\mu g.$  of N can be estimated, and 2  $\mu g.$  or greater amounts with accuracy. The method is applicable to protein hydrolysates. A. T. P.

**Colorimetric determination of serine.** M. J. Boyd and M. A. Logan (*J. Biol. Chem.*, 1942, **146**, 279—287).—The  $CH_2O$  formed by distillation of 1—5 mg. of serine (or of an acid hydrolysate of protein adjusted to the alkaline side of Me-red) with  $IO_4'$  is condensed with 1:3:6-(OH)<sub>2</sub> $C_{10}H_4(SO_3H)_2$  and measured colorimetrically with an error of 1—2%. Serine is slowly destroyed by acid hydrolysis and the determination is affected by the presence of carbohydrates unless completely converted into furfuraldehyde derivatives by hydrolysis. The following vals. for serine-N were obtained: horse hæmoglobin 4.42, dog hæmoglobin 4.22, collagen 3.22, ovalbumin 6.27, salmine 3.23, casein 4.75% of the total N. H. G. R.

**Possibility of differentiating between small amounts of cerebro-glucosides and -galactosides.** J. Brückner (*Z. physiol. Chem.*, 1942, **275**, 73—79).—1 c.c. of 0.01% sugar is mixed with 1 c.c. of orcinol reagent (2% in 20%  $H_2SO_4$ ) and floated on 3 c.c. of 92%  $H_2SO_4$ . The layers are mixed and the colour is observed immediately and after 8, 15, and 30 sec., stabilisation being sufficiently achieved by cooling in ice. Glucose and galactose (I) can thus be identified separately and their relative proportions can be determined in their mixtures. In the investigation of cerebro-galactosides and -glucosides impure preps. and organ extracts can be used provided that the carbohydrates are carefully removed. The lipid extract of human blood corpuscles shows the reactions of (I) and hence contains a cerebrogalactoside. H. W.

**Cryoscopic analysis of styrene, indene, and dicyclopentadiene.** E. H. Smoker and P. E. Burchfield (*Ind. Eng. Chem. [Anal.]*, 1943, **15**, 128—129).—Cryoscopy offers a precise analytical method for the determination of small quantities of impurities in styrene, indene, and dicyclopentadiene. Depressions of f.p. of these on addition of 0—4% of *p*-xylene are recorded, and molal dispersions are given. J. D. R.

**Determination of concentration of chlorophyll.** D. I. Saposhnikov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 369—371).—Chlorophyll (I) is determined from the width of the band I in the absorption spectrum, measured by a drum spectrometer, and the thickness of the solution layer. The widths of the bands are to each other as the square root of the respective amounts of (I). A. T. P.

## A., II.—Organic Chemistry

MAY, 1943.

## I.—ALIPHATIC.

**Double linking isomerisation in the preparation of straight-chained aliphatic olefines of higher mol. wt.** F. Asinger (*Ber.*, 1942, 75, [B], 1247—1259).— $\text{Al}_2\text{O}_3$  is obtained by pptn. of  $\text{AlCl}_3$  with aq.  $\text{NH}_3$ , washing the ppt. until Cl-free, peptisation with  $\text{HNO}_3$ , heating at  $450^\circ$ , grinding for 5 hr. with 20%  $\text{HNO}_3$ , and drying for 4 hr. at  $450^\circ$ . For dechlorinations this catalyst is heated in a Jena glass tube at  $250^\circ$  and the chloride, mixed with  $\text{N}_2$ , is passed over it.  $\alpha$ -Chloro-*n*-dodecane gives a dodecene mixture with ~5% of a dark green polymerisate. The mixture is ozonised and then quantitatively oxidised to acids by  $\text{Ag}_2\text{O}$  in alkaline suspension. The acids are separated by very slow fractional distillation. The hydrocarbon mixture contains  $\Delta^\alpha$ - 3.9,  $\Delta^\beta$ - 17.3,  $\Delta^\gamma$ - 19.4,  $\Delta^\delta$ - 20.3,  $\Delta^\epsilon$ - 19.4, and  $\Delta^z$ - 19.6 mol.-% dodecene. Dechlorination of cetyl chloride in like manner gives 25% of polymerides, cyclic compounds, olefines with the group  $\cdot\text{CH}_2\cdot\text{C}(\cdot\text{CH}_2)\cdot\text{CH}_2\cdot$  or  $\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot$ , and a mixture of hexadecenes:  $\Delta^\alpha$ - 0.8,  $\Delta^\beta$ - 4.8,  $\Delta^\gamma$ - 12.6,  $\Delta^\delta$ - 15.5,  $\Delta^\epsilon$ - 17.4,  $\Delta^z$ - 16.4,  $\Delta^v$ - 16.9,  $\Delta^w$ - 16.4 mol.-%.  $\alpha$ -Chloroheptadecane yields 25% of polymerisate and the following mol.-% of the heptadecenes:  $\Delta^\alpha$ - 1.0,  $\Delta^\beta$ - 1.25,  $\Delta^\gamma$ - 4.2,  $\Delta^\delta$ - 9.15,  $\Delta^\epsilon$ - 10.8,  $\Delta^z$ - 13.7,  $\Delta^v$ - 15.7,  $\Delta^w$ - 22.4,  $\Delta^x$ - 23.4. Dehydration of *n*-dodecanol by pure  $\text{Al}_2\text{O}_3$  at  $380^\circ$  gives 96% of a dodecene mixture containing  $\Delta^\alpha$ - 40.0,  $\Delta^\beta$ - 40.0,  $\Delta^\gamma$ - 7.9,  $\Delta^\delta$ - 2.0,  $\Delta^\epsilon$ - 0.75,  $\Delta^z$ - 0.35 mol.-%. With  $\text{Al}_2\text{O}_3$  activated by  $\text{HCl}$  the dodecene mixture contains  $\Delta^\alpha$ - 10.7,  $\Delta^\beta$ - 19.7,  $\Delta^\gamma$ - 16.8,  $\Delta^\delta$ - 17.6,  $\Delta^\epsilon$ - 17.3,  $\Delta^z$ - 19.3 mol.-%. If the catalyst is activated by  $\text{SiO}_2$  the dodecene mixture contains  $\Delta^\alpha$ - 10.7,  $\Delta^\beta$ - 18.3,  $\Delta^\gamma$ - 24.5,  $\Delta^\delta$ - 21.2,  $\Delta^\epsilon$ - 13.6,  $\Delta^z$ - 11.8 mol.-%. With a very active, pure  $\text{Al}_2\text{O}_3$  dehydration occurs at  $250^\circ$ , giving a dodecene mixture with  $\Delta^\alpha$ - 40.0,  $\Delta^\beta$ - 29.0,  $\Delta^\gamma$ - 11.7,  $\Delta^\delta$ - 8.15,  $\Delta^\epsilon$ - 6.10, and  $\Delta^z$ - 5.10 mol.-%. *n*-Dodecanol (3 mols.) and conc. syrupy  $\text{H}_3\text{PO}_4$  (3.5 mols.) are slowly heated to  $190^\circ$  and then at  $210$ — $220^\circ$ /600 mm., when the greater part of the olefine mixture distils. It contains  $\Delta^\alpha$ - 8.0,  $\Delta^\beta$ - 25.2,  $\Delta^\gamma$ - 25.2,  $\Delta^\delta$ - 17.9,  $\Delta^\epsilon$ - 13.0, and  $\Delta^z$ - 10.6 mol.-% dodecene. Technical samples of hexa- and octa-decene are shown to be mixtures of isomerides. A nearly homogeneous  $\Delta^\alpha$ -dodecene is obtained by dehydrogenating *n*-dodecanol by stearic acid at  $250^\circ$  and finally at  $330$ — $350^\circ$ /600 mm. The absence of isomerisation is not due to low temp. but to the absence of a catalyst. H. W.

**Isomerising action of anhydrous magnesium bromide on complex olefines with terminal double linking.** [Cetene =  $\Delta^\alpha$ -hexadecene.] F. Asinger (*Ber.*, 1942, 75, [B], 1260—1263).—A mixture of  $\Delta^\alpha$ - and  $\Delta^\beta$ -dodecene (mol. ratio, 97.64 : 2.36) is converted by boiling for 6 hr. with  $\text{MgBr}_2$  in  $\text{C}_6\text{H}_6$  into a mixture of  $\Delta^\alpha$ - 83.41,  $\Delta^\beta$ - 10.0,  $\Delta^\gamma$ - 4.20,  $\Delta^\delta$ - 2.24,  $\Delta^\epsilon$ - 0.42 mol.-% dodecene. The author does not therefore share the view of Suida *et al.* (*A.*, 1943, II, 78) that "it is very unlikely that isomerisations occur during the Grignard synthesis since high temp. are avoided" and does not consider the proof of the homogeneity of cetene to be valid. H. W.

**Rôle of neighbouring groups in replacement reactions.** I. Retention of configuration in the reaction of dihalides and acetoxyhalides with silver acetate. II. Effects of small amounts of water on the reaction of silver acetate in acetic acid with butene and cyclohexene derivatives. S. Winstein and R. E. Buckles. III. Retention of configuration in the reaction of  $\gamma$ -bromobutan- $\beta$ -ols with phosphorus tribromide. IV. Identity of various preparations of 1 : 2-dibromocyclohexane. S. Winstein. V. Effect of the neighbouring acetoxy group on the course of the replacement of the *p*-toluenesulphonate group of *trans*-2-acetoxycyclohexyl *p*-toluenesulphonate. S. Winstein, H. V. Hess, and R. E. Buckles (*J. Amer. Chem. Soc.*, 1942, 64, 2780—2786, 2787—2790, 2791—2792, 2792—2795, 2796—2801).—I. Interaction of *erythro*- or *threo*- $\text{CHMeBr}\cdot\text{CHMe}\cdot\text{OAc}$ , *meso*- or *dl*- $(\text{CHMeBr})_2$ , *dl*-*trans*-2-bromo-1-acetoxycyclohexane, or *dl*-*trans*-1 : 2-dibromocyclohexane (I) with  $\text{AgOAc}$  gives  $(\text{CHMe}\cdot\text{OAc})_2$  or 1 : 2-diacetoxycyclohexane (II), respectively, with almost complete (>87—98%) retention of configuration. Optically active  $(\text{CHMeBr})_2$  and *trans*-2-bromo-1-acetoxycyclohexane give completely inactive products. The reactions, considered to be of  $\text{S}_{\text{N}}1$  type, probably involve a double inversion. The steric results are ascribed

to production of intermediates,  $\text{>C}\begin{smallmatrix} \text{Br}^+ \\ \diagup \quad \diagdown \end{smallmatrix}\text{C}<$  (A) and (B). The scope and results of reactions involving such intermediates are discussed.

II. Addition of  $\text{H}_2\text{O}$  (up to 1—2 mols.) in the above-mentioned reactions leads to increasing amounts of  $\text{OH}\cdot[\text{CHMe}]_2\cdot\text{OAc}$  and

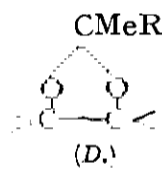


1-hydroxy-2-acetoxycyclohexane (III) (up to 64—72%) and inversion (up to 95—98%). Under the conditions of these reactions the monoacetates are converted to a considerable extent into diacetates but the diacetates are hardly affected. The bromohydrins which might be intermediates do not react similarly and configuration is mainly retained. Thus, the OH is introduced only after the first OAc. The formation of the monoacetate involves (B) and thence the orthoacetate (C), which then loses a proton and undergoes ring-fission without inversion; the single inversion thus occurs in formation of (B). Similar reactions are discussed.

III. *erythro*- and *threo*- $\text{CHMeBr}\cdot\text{CHMe}\cdot\text{OH}$  with  $\text{PBr}_3$  give  $(\text{CHMeBr})_2$  with 95% and ~90%, respectively, of retention of configuration. Reaction thus proceeds by way of (A).

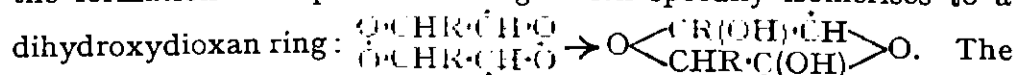
IV. (I) obtained from cyclohexene (IV) is also obtained from (i) cyclohexene oxide (V), 2-bromocyclohexanol [prep. from (IV) or 2-bromocyclohexanone], 2-bromocyclohexyl *p*-toluenesulphonate, or *cis*-(II) by fuming  $\text{HBr}$ , (ii) from 2-bromocyclohexanol [prep. from (V)] by  $\text{PBr}_3$ , or (iii) *cis*- or *trans*-(II) by  $\text{HBr}\cdot\text{AcOH}$ . (I) is considered to be the *trans*-compound. Formation of (B) favours formation of *trans*-dihalide in nucleophilic replacement reactions.

V. *trans*-2-Acetoxycyclohexyl *p*-toluenesulphonate (VI) with  $\text{KOAc}\cdot\text{AcOH}$  gives 93%-pure *trans*-(II), but addition of  $\text{H}_2\text{O}$  gives increasing amounts of inversion and *cis*-(III). In  $\text{EtOH}$  containing  $\text{CaCO}_3$  and a trace of  $\text{H}_2\text{O}$ , (VI) gives a product hydrolysed to *cis*-glycol, and in  $\text{EtOH}\cdot\text{KOAc}$  gives *cis*-(III). In  $\text{AcOH}$  (no  $\text{KOAc}$ ), *cis*-(II) is formed. Reactions proceed by way of (B). Formation of the *cis*-compounds involves (D) ( $\text{R} = \text{OEt}$  or  $\text{OAc}$ ).



**Dehydration of alcohols.** XIX. *tert*-Amyl alcohol and the related dimethylnepentylcarbinol. F. C. Whitmore, C. S. Rowland, S. N. Wrenn, and G. W. Kilmer (*J. Amer. Chem. Soc.*, 1942, 64, 2970—2972; cf. *A.*, 1941, II, 347).—Distillation of  $\text{CMe}_2\text{Et}\cdot\text{OH}$  from 15%  $\text{H}_2\text{SO}_4$  gives a 7 : 1 mixture of  $\text{CHMe}\cdot\text{CMe}_2 + \text{CH}_2\cdot\text{CMeEt}$ , but that of  $\text{CH}_2\text{Bu}^\gamma\cdot\text{CMe}_2\cdot\text{OH}$  gives a 1 : 4.5 mixture of  $\text{CHBu}^\gamma\cdot\text{CMe}_2 + \text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\text{Bu}^\gamma$ . The large effect of the  $\text{Bu}^\gamma$  is noted. Passage of  $\text{CHMeBu}^\gamma\cdot\text{OH}$  over activated  $\text{Al}_2\text{O}_3$  gives good yields of  $\text{CH}_2\cdot\text{CHBu}^\gamma$ , but none if the  $\text{Al}_2\text{O}_3$  is made even slightly alkaline. R. S. C.

**Autoxidation of oxygen-active acids.** VI. Total analyses of the process of autoxidation of the methyl esters of linoleic and linolenic acid and the hexaenoic acid of cod-liver oil by means of magnesium alkyl halides and the nature of mol. multiplication. W. Treibs (*Ber.*, 1942, 75, [B], 1164—1180; cf. *A.*, 1943, II, 80).—OH, CO, and  $\alpha$ -oxido-groups react immediately and quantitatively with 1 mol. of  $\text{MgMeI}$  in each case.  $\text{CO}_2\text{Me}$  of the higher fatty acids reacts somewhat more slowly but the change is invariably complete after 10 min. at  $20$ — $25^\circ$  or 1 min. at  $80^\circ$  and requires 2  $\text{MgMeI}$ . Tetrahydronaphthalene, cyclohexene (I), and  $\Delta^3$ -menthene H peroxide behave like OH-ketones, requiring 2 mols. of  $\text{MgMeI}$  and evolving 1 mol. of  $\text{CH}_4$ . The second mol. of  $\text{MgMeI}$  essentially oxidises (I) to cyclohexenol. With  $\text{MgPhBr}$  the main secondary product is  $\text{Ph}_2$ . With ascaridole the total requirement of  $\text{MgMeI}$  is invariably ~2 mols. and with rising temp. there is an evolution of  $\text{CH}_4$  approaching a limiting val. of 1 mol. In the analysis of the oils the sample is treated with a known excess of  $\text{MgMeI}$ .  $\text{CH}_4$  evolved immediately is measured and after a suitable interval the unchanged reagent is decomposed by a suitable alcohol and the  $\text{CH}_4$  evolved is again measured. It is thus shown that the immediately occurring mol. enlargement of elaeostearic ester (II) is a dimerisation caused by the formation of a perdioxy ring which speedily isomerises to a dihydroxydioxan ring:



The Me esters of linoleic, linolenic, and the hexaenoic acid of cod-liver oil are first converted into a labile, monomeric monoperoxide the  $\text{O}_2\text{H}$  group of which does not directly participate in the following

mol. enlargement of which it is essentially a preliminary. The actual enlargement occurs in precisely the same manner as with (II), a labile peroxidan ring being formed which passes spontaneously into a dihydroxydioxan ring. The most important phase of auto-oxidation, the multiplication of the mol., occurs in the same manner with all O-active acids. The most characteristic difference is that in (II) the intermol. directive forces required for the formation of the dimeric peroxide bridge are already present in virtue of the conjugated system whereas in the other esters they must be created by the monomeric monoperoxide stage. H. W.

**Lower hydrates of soap.** M. J. Buerger, L. B. Smith, A. de Bretteville, jun., and F. V. Ryer (*Proc. Nat. Acad. Sci.*, 1942, **28**, 526—529).—Evidence, which includes X-ray powder photographs, is presented which shows that soap forms previously considered to be anhyd. are hydrates of Na stearate with  $\frac{1}{2}$  and  $\frac{1}{3}$  mol.  $H_2O$  per mol. (See also A., 1943, I, 117.) J. L. E.

**Alkylation of linseed oil.** J. G. Smull and J. S. Saylor (*J. Amer. Chem. Soc.*, 1942, **64**, 3054).—When the Me esters obtained from linseed oil by MeOH are treated with NaOEt-EtOH at 60° and then with EtI, first at room temp. and then at 90°, the product, b.p. 205°/14 mm., is considered to be alkylated ( $\cdot CH \cdot CHEt \cdot CH \cdot$ ) because of its reduced I val. (average 177.4) and failure to give the fulvene reaction. R. S. C.

**Macrocyclic ring systems. I. Preparation and cyclisation of  $\omega$ -halogenoacylacetic esters.** H. Hunsdiecker (*Ber.*, 1942, **75**, [B], 1190—1197).—The action of NaOAlk on RHal·CO·CHAc·CO<sub>2</sub>Et (I) may follow the courses: (I)  $\rightarrow$  RHal·CO·CH<sub>2</sub>·CO<sub>2</sub>Me and thence  $\rightarrow$   $[R \cdot CO \cdot \dot{C}H \cdot CO_2Me]_n$  or  $\begin{matrix} R \\ \diagup \\ CO \end{matrix} > CH \cdot CO_2Me$  or OMe·R·CO·CH<sub>2</sub>·CO<sub>2</sub>Me; (I)  $\rightarrow$  OMe·R·CO·CHAc·CO<sub>2</sub>Et. The relative probabilities are estimated by measurement of the rates of fission of Et hexoylacetoacetate, of condensation of  $n$ -C<sub>6</sub>H<sub>13</sub>Br with CHAcNa·CO<sub>2</sub>Et, and of ether formation from NaOMe and Bu<sup>a</sup>Br. The first change is certainly complete within 90 min. whilst in the same time the second and third changes have proceeded to the extent of  $\sim 1\%$  and  $\sim 3\%$ , respectively. In harmony, the fission of halogenoacylacetoacetates proceeds very smoothly without disturbing side or consequent changes. An exception is furnished by Et  $\delta$ -bromovalerylacetoacetate, which gives a mixture of  $\sim 40\%$  of Et  $\delta$ -bromovalerate and  $\sim 60\%$  of Me cyclohexan-2-one-1-carboxylate.  $\mu$ -Bromotridecoic acid is converted (SOCl<sub>2</sub>) into its chloride, which is condensed with CHAcNa·CO<sub>2</sub>Et in Et<sub>2</sub>O to a product transformed by NaOMe-MeOH at room temp. into Me  $\beta$ -keto- $\chi$ -bromopentadecate, m.p. 47° (yield 67%); the corresponding I-compound (II) has m.p. 56.5°. Me  $\beta$ -keto- $\kappa$ -bromoundecate, b.p. 158°/1 mm. (Cu compound, m.p. 126°), and Me  $\beta$ -keto- $\nu$ -bromotridecoate, b.p. 185°/4 mm., m.p. 34.5° (corresponding I-compound, m.p. 46°), are obtained similarly. Very gradual addition of (II) to a boiling suspension of anhyd. K<sub>2</sub>CO<sub>3</sub> in boiling COMeEt affords Me cyclotetradecan-2-one-1-carboxylate, b.p. 145°/1.5 mm. (semicarbazone, m.p. 186—188°), converted by 80% H<sub>2</sub>SO<sub>4</sub> at room temp. into cyclotetradecanone, m.p. 52° (semicarbazone, m.p. 198°). H. W.

**Mechanism of the Diels-Alder reaction.** R. B. Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 3054—3059).—This reaction occurs by ionisation of the two components (cf. Weiss, A., 1942, II, 229), reversible formation of an intermol. semipolar linking,  $[A^+][B^-]$ , and finally irreversible formation of the product. Donor or acceptor mols.  $[NPhMe_2, s-C_6H_3(NO_2)_3]$  may be catalytic. R. S. C.

**Use of formaldehyde and 2:6-dichlorophenol-indophenol in determination of ascorbic and dehydroascorbic acid.**—See A., 1943, III, 258.

**Determination of ascorbic acid based on use of standardised 2:6-dichlorophenol-indophenol in xylene.**—See A., 1943, III, 257.

**Mercaptals and mercaptols of  $\beta$ -thiolpropionic acid.** B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1942, **15**, A, No. 8, 15 pp.).—Mercaptals from SH·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H (I) and the following aldehydes are described: CH<sub>2</sub>O, m.p. 142—143°, MeCHO, m.p. 62—63° (decomp.), EtCHO, m.p. 93—94.5°, CHO·CO<sub>2</sub>H, m.p. 131—132°, PhCHO, m.p. 88—89.5°, 4:3:1-OH·C<sub>6</sub>H<sub>3</sub>(OMe)·CHO, m.p. 123—124°, 3:4:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO, m.p. 85—88°, 3:4:1-CH<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·CHO, m.p. 104—105°, CH<sub>2</sub>Ph·CHO, m.p. 109—110°, Ph·[CH<sub>2</sub>]<sub>2</sub>·CHO, m.p. 72—73°, CHPh·CH·CHO, m.p. 93—95°, and furfuraldehyde, m.p. 87—88°. Mercaptols from (I) and the following ketones are prepared: COMe<sub>2</sub>, m.p. 88—89°, COMeEt, m.p. 53—54°, COEt<sub>2</sub>, m.p. 97—98°, AcCO<sub>2</sub>H, m.p. 147—148° (semi-mercaptol, m.p. 91.5—92°, first formed), CH<sub>2</sub>Ac·CO<sub>2</sub>H, m.p. 129—130° (decomp.) (from CH<sub>2</sub>Ac·CO<sub>2</sub>Et), Ac·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H, m.p. 142—143°, cyclohexanone, m.p. 96—97°, COPhMe, m.p. 111—112°, CH<sub>2</sub>Ph·COMe, m.p. 117—118°, COPh<sub>2</sub>, m.p. 147.5—148.5°, BzCO<sub>2</sub>H, m.p. 161—162° (decomp.). Arabinose did not react. M. H. M. A.

**Direct introduction of the chloroformyl (·COCl) group into acid chlorides.**—See A., 1943, II, 134.

**Condensations. XVIII. Acylation of the anions of certain esters with ethyl carbonate.** C. R. Hauser, B. Abramovitch, and J. T. Adams (*J. Amer. Chem. Soc.*, 1942, **64**, 2714—2715; cf. A., 1943,

II, 81).—Adding Bu<sup>a</sup>OAc and then Et<sub>2</sub>CO<sub>3</sub> to NaCPh<sub>3</sub>-Et<sub>2</sub>O-N<sub>2</sub> gives Et Bu<sup>a</sup> malonate (54%), b.p. 93—95°/17 mm. Bu<sup>a</sup> propionate (prep. from Bu<sup>a</sup>OH and EtCOCl in NPhMe<sub>2</sub>; 63% yield), b.p. 118—118.5°, gives similarly Et Bu<sup>a</sup> methylmalonate (72%), b.p. 94—95°, and CH<sub>2</sub>Bu<sup>a</sup>·CO<sub>2</sub>Et gives Et<sub>2</sub> tert.-butylmalonate [Et  $\alpha$ -carbethoxy- $\beta\beta$ -dimethyl-n-butyrate] (47%), b.p. 102—104°/11 mm. R. S. C.

**Preparation of ethyl ethylmalonate and  $\Delta^1$ -cyclohexenylmalonate from the corresponding oxaloacetates.**—See A., 1943, II, 133.

**Dipole moments of diethyl esters of substituted malonic acids, and of glyptals.**—See A., 1943, I, 116.

**Alkylsuccinic acids. II.  $n$ -Amyl- and  $n$ -decyl-succinic acids.** S. U. Mehta and K. S. Nargund (*J. Univ. Bombay*, 1942, **11**, A, Part 3, 134—135; cf. A., 1942, II, 278).— $n$ -Heptane- $\alpha\beta$ -tricarboxylic acid, m.p. 134—135°, at 190° yields  $n$ -amylsuccinic acid, m.p. 81—82° (anhydride, b.p. 140°/13 mm.; monoanilide, m.p. 112—115°; mono- $p$ -toluidide, m.p. 122—124°).  $n$ -Dodecane- $\alpha\beta$ -tricarboxylic acid, m.p. 135°, yields  $n$ -decylsuccinic acid, m.p. 94—95° (anhydride, m.p. 70—71°; monoanilide, m.p. 103—104°; Et<sub>2</sub> ester, b.p. 175—180°/13 mm.). A. Li.

**Mechanism of photolysis of propaldehyde.**—See A., 1943, I, 133.

**Keto-ethers. X.  $\alpha$ -Methoxyethyl alkyl ketones.** W. P. Wallace and H. R. Henze (*J. Amer. Chem. Soc.*, 1942, **64**, 2882; cf. A., 1942, II, 300).—MeOH (I), paraldehyde (1 equiv.), and dry HCl give CHMeCl·OMe (95%), b.p. 70—72°/746 mm., converted in dry Et<sub>2</sub>O into OMe·CHMe·CN (36%), b.p. 117—119°/740 mm., which with MgRBr in Et<sub>2</sub>O gives 13—63% of Me, b.p. 115—116°/739 mm. (141°), and Et  $\alpha$ -methoxyethyl ketone, b.p. 135—136°/750 mm. (120.5°), OMe·CHMe Pr<sup>a</sup>, b.p. 154—155°/746 mm. (169°), Pr<sup>a</sup>Pr<sup>a</sup>, b.p. 57—58°/31 mm. (146°), Bu<sup>a</sup>, b.p. 81—82°/36 mm. (154°), Bu<sup>a</sup>Pr<sup>a</sup>, b.p. 51—52°/9 mm. (145°), sec.-Bu, b.p. 76—77°/36 mm. (127°), Bu<sup>a</sup>Pr<sup>a</sup>, b.p. 54—64°/34 mm. (121°),  $n$ -, b.p. 60—61°/3 mm. (144°), and iso-amyl ketone, b.p. 64—65°/6 mm. (154.5°), figures in parentheses being m.p. of the semicarbazones. M.p. are corr. R. S. C.

**Catalytic interchange of groups in aliphatic amines.**—See A., 1943, I, 132.

**Preparation of mixed sec. aliphatic amines, NHRR'. H. R. Henze and D. D. Humphreys (*J. Amer. Chem. Soc.*, 1942, **64**, 2878—2880).—Condensation of NH<sub>2</sub>Bu<sup>a</sup> with the appropriate ketone or aldehyde and hydrogenation (Raney Ni; 75°/3000 lb.; cf. A., 1940, II, 222) of the crude product gives 31—52% of NH<sub>2</sub>EtBu<sup>a</sup>, b.p. 111—112°/747 mm., NHPr<sup>a</sup>Bu<sup>a</sup>, b.p. 138—139°/745 mm., iso-propyl- $n$ -butylamine, b.p. 124—125°/748 mm.,  $n$ -butyl-isobutyl-, b.p. 150—151°/738 mm., sec.-butyl-, b.p. 149—149.5°/751 mm.,  $n$ -amyl-, b.p. 180—182°/743 mm., and isoamyl-amine, b.p. 175—177°/745 mm. NH<sub>2</sub>Me and Pr<sup>a</sup>CHO lead to NHMeBu<sup>a</sup> (26%), b.p. 89—91°/750 mm., and NMeBu<sup>a</sup><sub>2</sub>. CH<sub>2</sub>Br·COMe (I) and NHBu<sup>a</sup>R (2 mols.) in Et<sub>2</sub>O give 41—74% of  $N$ -methyl-, b.p. 76°/19 mm. (104—104.5°), ethyl-, b.p. 87—88°/17 mm. (126.5—127.5°),  $n$ -, b.p. 90—91°/12 mm. (130.5—131°), and iso-propyl-, b.p. 92—94.5°/13 mm. (151—152°),  $N$ -butylaminoacetone,  $N$ - $n$ -butyl- $N$ -iso-, b.p. 106—107°/14 mm. (139—139.5°), and sec.-butyl-, b.p. 105—106°/12 mm. (172—172.5°),  $n$ -, b.p. 110—111°/6 mm. (107.5—108.5°), and iso-amyl-, b.p. 80—82°/3 mm. (116—117°), aminoacetone, figures in parentheses being m.p. of the semicarbazones. Picrates and hydrochlorides were oils. Other physical data of the products are recorded. M.p. and b.p. are corr. R. S. C.**

**Azides of organic bases.** A. Cirulis and M. Straumanis (*J. pr. Chem.*, 1942, [ii], 161, 65—76).—NH<sub>2</sub>Me, HCl, NaN<sub>3</sub>, and H<sub>2</sub>O containing a little NH<sub>2</sub>Me at 100—150°, or 33% aq. NH<sub>2</sub>Me and HN<sub>3</sub> (from NaN<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>), give methylamine azide, m.p. 140°. Similarly prepared are ethyl-, m.p. 65°,  $n$ -propyl-, m.p. 85°,  $n$ -, m.p. 85°, and iso-butyl-, m.p. 115°, allyl-, dimethyl-, m.p. 74°, diethyl-, m.p. 48°, di- $n$ -propyl-, m.p. 101°, di- $n$ -, m.p. 143°, and isobutyl-, m.p. 135°, and di-isoamyl-amine azide, m.p. 176°, ethylene-[(CH<sub>2</sub>·NH<sub>2</sub>)<sub>2</sub>](N<sub>3</sub>)<sub>2</sub>, m.p. 172° (decomp.), and propylene-diamine azide, m.p. 166° (decomp.);  $\alpha\gamma$ -diaminopropan- $\beta$ -ol azide, m.p. 115°; guanidine, m.p. 46°, and amidoguanidine azide, m.p. 123°; benzylamine, m.p. 157°, piperidine, m.p.  $\sim 60^\circ$  (decomp.), aminocyclohexane, m.p. 112—113°, piperazine, m.p. 180—181°, and "nitron" azide, decomp. 160°. A. T. P.

**Muscarine. II.** F. Kögl and H. Veldstra [and, in part, P. J. van der Laan] (*Annalen*, 1942, **552**, 1—36; cf. A., 1931, 1279).—Unsuccessful attempts are described to discriminate between the formulæ OH·CH<sub>2</sub>·CH<sub>2</sub>·CH(NMe<sub>3</sub>·OH)·CHO and OH·NMe<sub>3</sub>·CH<sub>2</sub>·CH<sub>2</sub>·CH(OH)·CHO for muscarine (I). Passage of Br vapour through CHMe·CH·CHO in 75% aq. MeOH at  $<0^\circ$  gives  $\alpha$ -bromo- $\beta$ -methoxybutaldehyde (II), b.p. 56.5°/1.8 mm., oxidised by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and dil. H<sub>2</sub>SO<sub>4</sub> to  $\alpha$ -bromo- $\beta$ -methoxybutyric acid, m.p. 60°, which is transformed by KOH-EtOH into OMe·CMe·CH·CO<sub>2</sub>H, m.p. 128.5°, hydrolysed by dil. H<sub>2</sub>SO<sub>4</sub> at 100° to COMe<sub>2</sub>. NHMe<sub>2</sub> in cold Et<sub>2</sub>O converts (I) into  $\alpha$ -dimethylamino- $\beta$ -methoxybutaldehyde, b.p. 34—35°/0.6 mm., which in MeOH gives the methiodide, m.p. 160—161°, which reduces Fehling's solution but colours magenta-H<sub>2</sub>SO<sub>4</sub> slowly if at all. It is transformed into the corresponding hygroscopic chloride, m.p. 130°, softens at 125° (aurichloride, m.p.

**70.** *reineckate*, and *aurichloride*, m.p. 116° (decomp.).  $\text{CHEt}:\text{CH}:\text{CO}_2\text{H}$  similarly affords  $\alpha$ -bromo- $\beta$ -methoxy-*n*-valeraldehyde, b.p. 58—60°/0.85 mm., and thence  $\alpha$ -dimethylamino- $\beta$ -methoxy-*n*-valeraldehyde, b.p. 40—42°/0.4 mm. [*methiodide*, m.p. 186—187° (decomp.)]; *reineckate*; *aurichloride*, m.p. 148° (decomp.). Pharmacologically these compounds are inactive on the isolated frog heart in comparison with (I). Gradual addition of HOCl to  $\text{CHEt}:\text{CH}:\text{CO}_2\text{H}$  in  $\text{H}_2\text{O}$  at 0° leads to  $\alpha$ -chloro- $\beta$ -hydroxy-*n*-valeric acid (II), b.p. 139°/3 mm., m.p. 66° (*Et* ester, b.p. 92°/2 mm.; *Ac* derivative, m.p. 99°); these substances do not give homogeneous products with  $\text{NMe}_3$ . (I) is converted by NaOH in aq. EtOH into  $\alpha$ - $\beta$ -epoxy-*n*-valerate, transformed by 33%  $\text{NHMe}_2$  at 100° into  $\beta$ -dimethylamino- $\alpha$ -hydroxy-*n*-valeric acid (III), m.p. 200° (decomp.), also obtained from (II) and 33%  $\text{NHMe}_2\cdot\text{C}_6\text{H}_5$  at 100°. (III) is oxidised by  $\text{Pb}(\text{OAc})_4$  in  $\text{AcOH}$  to  $\alpha$ -dimethylamino-*n*-butaldehyde, b.p. 44—45°/18 mm., which strongly reduces Fehling's solution; the corresponding *methiodide*, m.p. 185—186°, reduces warm Fehling's solution but does not give a colour with magenta- $\text{H}_2\text{SO}_4$ . *Crotonaldehyde Me\_2 acetal*, b.p. 116—119°, and HOCl in  $\text{H}_2\text{O}$  at 0° afford  $\alpha$ -chloro- $\beta$ -hydroxy-*n*-butaldehyde *Me\_2 acetal*, b.p. 78°/0.6 mm., which with NaI and 33%  $\text{NHMe}_2\cdot\text{MeOH}$  at 100° yields  $\beta$ -dimethylamino- $\alpha$ -hydroxy-*n*-butaldehyde *Me\_2 acetal*, b.p. 80°/0.5 mm., m.p. ~30°; this gives a non-cryst. *methiodide* and *methochloride* (IV) (corresponding *aurichloride*, m.p. 90°). (IV) is hydrolysed by conc. HCl at room temp. to the non-cryst. aldehyde *methochloride* (corresponding *aurichloride*, m.p. 195—196°).  $\alpha$ -Bromo-*n*-valeraldehyde *Me\_2 acetal*, b.p. 94°/30 mm. (corresponding *Et\_2 acetal*, b.p. 97°/23 mm.), is converted into  $\Delta^2$ -pentenal *Me\_2 acetal*, b.p. 68°/45 mm. (*Et\_2 acetal*, b.p. 62°/16 mm.), which gives  $\alpha$ -chloro- $\beta$ -hydroxy-*n*-valeraldehyde *Me\_2 acetal*, b.p. 71°/0.3 mm. (*Et\_2 acetal*, b.p. 88°/0.3 mm.), and thence  $\beta$ -dimethylamino- $\alpha$ -hydroxy-*n*-valeraldehyde *Me\_2 acetal* (V), b.p. 77°/0.3 mm. [*Et\_2 acetal* (VI), b.p. 86°/0.3 mm.]. (V) gives a non-cryst. *methiodide* and *methochloride* (corresponding *aurichloride*, m.p. ~90°) whilst (VI) yields a *methiodide*, m.p. 125°, converted into the *methochloride* (*aurichloride*, m.p. ~90°).  $\beta$ -Dimethylamino- $\alpha$ -hydroxy-*n*-valeraldehyde *methochloride* reduces Fehling's solution and fairly readily gives a violet colour with magenta- $\text{H}_2\text{SO}_4$ ; the corresponding *reineckate* is cryst. but the m.p. of the *aurichloride*, ~175°, varies with different specimens. Dipropenyl glycol is oxidised by  $\text{BzO}_2\text{H}$  in light petroleum (b.p. 40—60°) to  $\beta$ - $\gamma$ - $\eta$ -diepoxyoctane- $\delta\epsilon$ -diol (VII), m.p. 138—140°, with some  $\beta$ - $\gamma$ -epoxyoctane- $\delta\epsilon$ - $\zeta\eta$ -tetraol, m.p. 178°. (VII) is oxidised by  $\text{Pb}(\text{OAc})_4$  in warm  $n\text{-C}_5\text{H}_{12}$  to  $\beta$ - $\gamma$ -epoxybutanol, b.p. 87—88°/400 mm., which liberates I from KI in  $\text{AcOH}$ . It is slowly transformed by 15%  $\text{NHMe}_2\cdot\text{H}_2\text{O}$  into  $\beta$ -dimethylamino- $\alpha$ -hydroxy-*n*-butaldehyde, converted through the non-cryst. *methiodide* into the *reineckate* and thence into a non-homogeneous *aurichloride*.

The isolation of (I) from toadstool has been improved. In  $\text{AcOH}$  muscarine chloride has the simple mol. wt. *Muscarine aurichloride* has m.p. 115—117°. H. W.

**Glucosamine.**  $\alpha$ - and  $\beta$ -Glucosamine and penta-acetylglucosamine. O. Westphal and H. Holzmänn [with E. Reiche] (*Ber.*, 1942, 75, [B], 1274—1282).—The action of  $\text{NEt}_3$  and EtOH on a suspension of powdered glucosamine hydrochloride (I) from lobster shells ( $\alpha$ -form) for 2 days at as low a temp. as possible followed by 3 or 4 similar treatments with decreasing amounts of  $\text{NEt}_3$  gives  $\alpha$ -glucosamine (II), m.p. 88° (corr.),  $[\alpha]_D^{20} +100^\circ$  to  $+47.5^\circ$  (equilibrium val.) in  $\text{H}_2\text{O}$  in 30 min. The mutarotation is ~50 times as rapid as that of glucose. Similar treatment of (I) with  $\text{NHEt}_2$  leads to  $\beta$ -glucosamine (III), m.p. 110—111° (corr.),  $[\alpha]_D^{20} +28^\circ$  to  $+47.5^\circ$  (equilibrium val.) in  $\text{H}_2\text{O}$  in 30 min. Thus obtained (III) is not quite homogeneous. In EtOH containing piperidine at 40° and at 60° there is a gradual conversion of (II) into (III), which itself undergoes chemical alteration. In contact with abs. EtOH at 40° there is a complete conversion of (II) into pure (III) and by this method (III) as obtained above is converted into the homogeneous material, m.p. 120° (corr.),  $[\alpha]_D^{20} +14^\circ$  to  $+47.5^\circ$  (equilibrium val.) in  $\text{H}_2\text{O}$  in 30 min. (II) is transformed by prolonged contact with  $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$  at room temp. into  $\alpha$ -penta-acetylglucosamine (IV), m.p. 139°,  $[\alpha]_D^{20} +92.0^\circ$  in  $\text{CHCl}_3$ , whilst under similar conditions (III) gives  $\beta$ -penta-acetylglucosamine (V), m.p. 186°. (III) is converted by  $\text{Ac}_2\text{O}$  and  $\text{C}_5\text{H}_5\text{N}$  containing a little  $\text{NEt}_3$  into a mixture of (IV) and (V). H. W.

**NN-Di-*n*-butylhydroxylamine and its oxalate.** V. H. Dermer and O. C. Dermer (*J. Amer. Chem. Soc.*, 1942, 64, 3057).—Adding  $\text{NO}_2$  in  $\text{Et}_2\text{O}$  to well-stirred  $\text{MgBu}^a\text{Br}$  in  $\text{Et}_2\text{O}$  gives NN-di-*n*-butylhydroxylamine, m.p. 52.5—53° (reduces Ag,  $\text{Cu}^{\text{II}}$ , and  $\text{Au}^{\text{III}}$ ), isolated as oxalate, m.p. 144—144.5°, which can be titrated as free acid. R. S. C.

**Oxidation of geometrically isomeric platinoglycines.** A. A. Grunberg (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 32, 57—58).— $\text{K}_2\text{PtCl}_6$  and *cis*-( $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2$ ) $_2\text{Pt}$  give yellow crystals of *cis*- $\text{Pt}(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2\text{Cl}_2$ ; the *trans*-form is similarly obtained: the configurations are proved by reduction with  $\text{K}_2\text{C}_2\text{O}_4$ . F. R. S.

**Benzoylation and resolution of alanine.** M. Levy and A. H. Palmer (*J. Biol. Chem.*, 1942, 146, 493—495).—A modification in the prep. of benzoyl-*dl*-alanine by  $\text{BzCl}$  and NaOH and its resolution

by brucine and strychnine are described. The equation  $[\alpha]_D = 35.2^\circ + 1.0c$  ( $c$  = concn. in g. per 10 ml.) expresses the optical activity of benzoylalanine in one equiv. of alkali. Alanine in excess of HCl has  $[\alpha]_D^{25} 14.5^\circ$ , the sign of the rotation being opposite in sense to the configuration. The equations of Pacsu and Mullen (*A.*, 1941, II, 36) should be discarded. W. McC.

**Interaction of formaldehyde with *l*(-)-asparagine.** D. C. Carpenter and F. E. Lovelace (*J. Amer. Chem. Soc.*, 1942, 64, 2899—2902).—Interaction of *l*-asparagine (I) + NaOH (1 mol.) with varying amounts of  $\text{CH}_2\text{O}$  is followed by determination of pH,  $\alpha$ , and unchanged  $\text{CH}_2\text{O}$ . (I) reacts first with 1 mol. of  $\text{CH}_2\text{O}$  to give the  $\text{CH}_2$  compound and then with a second mol. to give a compound of unknown structure which readily loses  $\text{CH}_2\text{O}$ . R. S. C.

**Oxidation of amino-acids by hydrogen peroxide in formic acid.** G. Toennies and R. P. Homiller (*J. Amer. Chem. Soc.*, 1942, 64, 3054—3056).— $\text{H}_2\text{O}_2$  in 88%  $\text{HCO}_2\text{H}$  forms the max. amount of  $\text{HCO}_2\text{H}$  in 1 hr. at room temp. This reagent rapidly oxidises *dl*-methionine (2.05 O consumed; sulphone formed), *dl*-cystine (5.25 O consumed; cysteic acid formed), and *l*-tryptophan (3.05 O consumed; ? product), but only very slowly affects 16 other  $\text{NH}_2$ -acids. R. S. C.

**Synthesis of peptides of *l*-serine.** J. S. Fruton (*J. Biol. Chem.*, 1943, 146, 463—470).—*l*-Serine,  $[\alpha]_D^{25} +14.8^\circ$  in 2*N*-HCl, or its Me ester, and  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{COCl}$ , give carbobenzyloxy-*l*-serine, m.p. 121°,  $[\alpha]_D^{25} +5.6^\circ$  in  $\text{AcOH}$ , or its Me ester, and thence carbobenzyloxy-*l*-serinehydrazide (I), m.p. 181°, and *l*-serinamide (II), m.p. 132—133°,  $[\alpha]_D^{25} +14.4^\circ$  in EtOH. (I) is converted into the azide (III), which in dry EtOAc with  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{CH}_2\text{Ph}$  in  $\text{Et}_2\text{O}$  at room temp. affords carbobenzyloxy-*l*-serylglycine  $\text{CH}_2\text{Ph}$  ester, m.p. 102°, hydrogenated (Pd-C; MeOH) to *l*-serylglycine,  $[\alpha]_D^{25} +30.2^\circ$  in *N*-HCl. The latter is also obtained by hydrogenating carbobenzyloxy-*l*-serylglycine, m.p. 131°, prepared from its *Et* ester, m.p. 105—107°, and *N*-NaOH-MeOH at room temp. (III) and *l*-alanine Me ester give, through its Me ester, m.p. 113—114°, carbobenzyloxy-*l*-seryl-*l*-alanine (+0.5 $\text{H}_2\text{O}$ ), m.p. 161—162° after 3 hr. at 100° in vac.; hydrogenation yields *l*-seryl-*l*-alanine,  $[\alpha]_D^{25} -30.4^\circ$  in *N*-HCl. Also prepared from (III) are carbobenzyloxy-*l*-seryl-*l*-serine, m.p. 169—171° (Me ester, m.p. 143—145°), *l*-seryl-*l*-serine,  $[\alpha]_D^{25} +14.2^\circ$  in *N*-HCl, carbobenzyloxy-*l*-seryl-*l*-glutamic acid, m.p. 152—153° (*Et\_2* ester, m.p. 85—86°), and *l*-seryl-*l*-glutamic acid,  $[\alpha]_D^{25} -9.4^\circ$  in *N*-HCl. Partial hydrolysis of dipeptides containing *l*-serine occurs by aq. extract of swine intestinal mucosa at 40°. (II) is hydrolysed by cysteine-papain or by cysteine-ox spleen cathepsin; the hydrolysis follows the kinetics of a first order reaction. (III) in EtOAc at 40° gives 4-carbobenzyloxyamino-oxazolid-2-one, m.p. 171°, converted by 10% HCl into  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CO}\cdot\text{NH}_2$ . A. T. P.

**Tetranucleotide of yeast- and thymo-nucleic acid.**—See A., 1943, II, 143.

**Acrylonitrile. II. Reactions with ketones.** H. A. Bruson and T. W. Riener (*J. Amer. Chem. Soc.*, 1942, 64, 2850—2858; cf. A., 1943, II, 62).—In presence of a little  $\text{CH}_2\text{Ph}\cdot\text{NMe}_3\cdot\text{OH}$  (I) or KOH etc.,  $\text{CH}_2\text{CH}:\text{CN}$  (II) condenses with  $\text{COArMe}$  to give  $\text{COAr}\cdot\text{C}[(\text{CH}_2)_2\text{CN}]_3$  and thence the tricarboxylic acid, with numerous cyclic ketones, all the H adjacent to the CO being substituted, and with  $\text{COMe}\cdot\text{CH}_2\text{R}$  to give  $\text{COMe}\cdot\text{CR}[(\text{CH}_2)_2\text{CN}]_2$  and then some substitution in the Me. Dropping (II) into  $\text{COArMe}$  and a little (I) in dioxan or  $\text{Bu}^t\text{OH}$  at 25—40° gives  $\gamma$ -benzoyl-, m.p. 128—129°,  $\gamma$ -2-naphthoyl-, m.p. 122°,  $\gamma$ -*p*-phenylbenzoyl-, m.p. 178°,  $\gamma$ -*p*-anisoyl-, m.p. 133°,  $\gamma$ -*p*-toluoyl-, m.p. 161—162°,  $\gamma$ -mesitoyl-, m.p. 126°,  $\gamma$ -*p*-chlorobenzoyl-, m.p. 141—142°, and  $\gamma$ -*p*-bromobenzoyl-, m.p. 151—152°,  $\gamma$ - $\beta'$ -cyanoethylpimelodinitrile and thence (boiling aq. KOH) the corresponding tricarboxylic acids, m.p. 143—145°, 173—174°, 236—238°, 219°, 226°, —, 225—227°, and 241—243°, respectively.  $\text{COPhEt}$  and  $\text{COPh}\cdot\text{CH}_2\text{Ph}$  give similarly  $\gamma$ -benzoyl- $\gamma$ -methyl-, m.p. 66°, and  $\gamma$ -phenyl-pimelodinitrile, m.p. 149—150°, hydrolysed to the pimelic acids, m.p. 166—167° and 172—173°, respectively. The appropriate cyclic ketone in (I)-dioxan or  $\text{C}_6\text{H}_6$  or 40% aq. KOH- $\text{Bu}^t\text{OH}$  gives 1-keto-2 : 2-di- $\beta$ -cyanoethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 80°, 2 : 2 : 6-tri- $\beta$ -cyanoethyl-6-methylcyclohexanone, m.p. 69—70°, 2 : 2 : 5 : 5-tetra- $\beta$ -cyanoethylcyclopentanone, m.p. 175°, 2 : 2 : 6 : 6-tetra- $\beta$ -cyanoethyl-cyclohexanone, m.p. 165°, -4-methyl-, m.p. 138°, -4-tert.-amyl-, m.p. 145°, -4-aary-tetramethyl-*n*-butyl-, m.p. 155—156°, and -4-cyclohexyl-cyclohexanone, m.p. 223—224°, and 4 : 4-di- $\beta$ -cyanoethyl-2 : 2 : 5 : 5-tetramethyltetrahydrofuran-3-one, m.p. 153°, alkaline hydrolysis then yielding 2 : 2 : 5 : 5-tetra- $\beta$ -carboxyethylcyclopentanone, + $\text{H}_2\text{O}$ , m.p. 173°, 2 : 2 : 6 : 6-tetra- $\beta$ -carboxyethylcyclohexanone, m.p. 179—180°, -4-methyl-, m.p. 205—206°, -4-tert.-amyl-, m.p. 205°, -4-aary-tetramethyl-*n*-butyl-, m.p. 185—186°, and -cyclohexyl-cyclohexanone, m.p. 205—206°, and 4 : 4-di- $\beta$ -carboxyethyl-2 : 2 : 5 : 5-tetramethyltetrahydrofuran-3-one, m.p. 170—171°. With 1—2 mols. of (II), cyclohexanone gives 2- $\beta$ -cyanoethyl-, b.p. 138—142°/10 mm., and 2 : 2- (or 2 : 6)-di- $\beta$ -cyanoethyl-cyclohexanone, m.p. 69°.  $\text{CO}(\text{CH}_2\text{Ph})_2$  gives only a syrup, yielding, by hydrolysis,  $\gamma\epsilon$ -diphenyl- $\gamma$ - $\beta'$ -carboxyethyl-*n*-heptan- $\delta$ -one- $\gamma\eta$ -dicarboxylic acid, m.p. 205°; similarly,  $\text{COEt}_2$  gives only  $\alpha\eta$ -dicyano- $\gamma\epsilon$ -dimethyl- $\gamma$ - $\beta'$ -cyanoethyl-*n*-heptan- $\gamma$ -one, m.p. 90—91°, and thence

the *tricarboxylic acid*, m.p. 116°. COMeEt and (II) in KOH-MeOH-BuOH give  $\gamma$ -acetyl- $\gamma$ -methylpimelodinitrile (III), m.p. 67°, the structure of which is proved by hydrolysis to  $\gamma$ -acetyl- $\gamma$ -methylpimelic acid, m.p. 125°, which with KOCl-NaOH at 60–70° gives  $\text{CHCl}_3$  and  $\gamma$ -carboxy- $\gamma$ -methylpimelic acid, m.p. 111°. Further reaction of (III) with (II) gives  $\alpha$ -dicyano- $\gamma$ -methyl- $\gamma$ -di- $\beta'$ -cyanoethyl-n-heptan- $\delta$ -one, m.p. 84–85°. COMePr<sup>a</sup> and (II) give  $\gamma$ -acetyl- $\gamma$ -ethylpimelodinitrile (IV), m.p. 109°, and  $\alpha$ -dicyano- $\gamma$ -ethyl- $\gamma$ - $\beta'$ -cyanoethyl-n-heptan- $\delta$ -one, m.p. 90–91°. Hydrolysis of (IV) yields  $\gamma$ -acetyl-, m.p. 112–113°, and oxidation gives  $\gamma$ -carboxy- $\gamma$ -ethylpimelic acid, m.p. 172°. Similarly are obtained  $\gamma$ -acetyl- $\gamma$ -isopropyl-, m.p. 101°, b.p. 200–205°/2 mm.,  $\gamma$ -n-butyl-, m.p. 63°, b.p. 205–210°/2 mm., and  $\gamma$ -n-amyl-pimelodinitrile, m.p. 47°, b.p. 195–200°/1 mm.,  $\gamma$ -acetyl- $\gamma$ -isopropyl-, m.p. 148°,  $\gamma$ -n-butyl-, m.p. 60–61°, and  $\gamma$ -n-amyl-pimelic acid, m.p. 73–74°,  $\gamma$ -carboxy- $\gamma$ -isopropyl-, m.p. 160–161°,  $\gamma$ -n-butyl-, m.p. 125°, and  $\gamma$ -n-amyl-pimelic acid, m.p. 114–115°. COMe<sub>2</sub> yields  $\gamma$ -acetyl- $\gamma$ - $\beta'$ -cyanoethylpimelodinitrile (V), m.p. 154°, and then  $\alpha$ -dicyano- $\gamma$ -di- $\beta'$ -cyanoethyl-n-heptan- $\delta$ -one, m.p. 121–122°, and a resin containing perhaps  $(\text{CN} \cdot [\text{CH}_2]_5)_n$  compounds. (V) yields as above  $\gamma$ -acetyl-, m.p. 149–150°, and  $\gamma$ -carboxy- $\gamma$ - $\beta'$ -carboxyethylpimelic acid, softens 182°, m.p. 192°. COMe·CH<sub>2</sub>Ph gives  $\gamma$ -acetyl- $\gamma$ -phenylpimelodinitrile, m.p. 109–110°,  $\gamma$ -acetyl-, m.p. 171–172°, and  $\gamma$ -carboxy- $\gamma$ -phenylpimelic acid, m.p. 154°. CH<sub>2</sub>Ac·CO<sub>2</sub>R gives  $\gamma$ -acetyl- $\gamma$ -carbomethoxy-, m.p. 154°, and  $\gamma$ -carbomethoxy-pimelodinitrile, m.p. 82°. Camphor, isophorone, and COBu<sub>2</sub> do not react with (II). CH<sub>2</sub>:CMe·CN or CHMe:CH·CN cannot replace (II). R. S. C.

## II.—SUGARS AND GLUCOSIDES.

**Phosphorylations and reactions with triphenylmethyl chloride.** K. Zeile and W. Kruckenberg (*Ber.*, 1942, 75, [B], 1127–1140).—NHPH·POCl<sub>2</sub> and glucose 1:2:3:4-tetra-acetate in C<sub>6</sub>H<sub>5</sub>N at room temp. with subsequent addition of EtOH afford *Et tetra-acetylglucosidoanilino-N-phosphonate*, m.p. 116–117°,  $[\alpha]_D^{25} + 25^\circ$  in C<sub>6</sub>H<sub>6</sub>. In C<sub>6</sub>H<sub>5</sub>N (NHPH)<sub>2</sub>POCl (I) and (NHPH)<sub>2</sub>PO·OH give *pyrophosphor-tetra-anilide*, m.p. 222°, also obtained when a solution of (I) in C<sub>6</sub>H<sub>5</sub>N is pptd. by H<sub>2</sub>O. Cholesterol and NPh<sub>2</sub>·POCl<sub>2</sub> (1:1) in C<sub>6</sub>H<sub>5</sub>N at 100° yield *cholesteryl diphenylamine-N-phosphonate*, m.p. 173°, whereas the reactants (2:1) afford tetracholesteryl pyrophosphate, C<sub>108</sub>H<sub>184</sub>O<sub>8</sub>P<sub>2</sub>·2H<sub>2</sub>O, m.p. 208°. NPh<sub>2</sub>·POCl<sub>2</sub> and  $\alpha$ -methylglucoside in C<sub>6</sub>H<sub>5</sub>N at room temp. give 3:6-diphenylamine-N-phosphoryl- $\alpha$ -methylglucoside, m.p. 251°,  $[\alpha]_D^{18} - 18^\circ$  in C<sub>6</sub>H<sub>5</sub>N, which is converted by Ac<sub>2</sub>O in abs. C<sub>6</sub>H<sub>5</sub>N at room temp. into the 2:4-diacetate, m.p. 138°,  $[\alpha]_D^{21} - 80^\circ$  in C<sub>6</sub>H<sub>6</sub>, but does not react with CPh<sub>3</sub>Cl-C<sub>6</sub>H<sub>5</sub>N at 100°. Treatment of xylose with CPh<sub>3</sub>Cl and C<sub>6</sub>H<sub>5</sub>N at 100° gives a product which cannot be worked up successfully by crystallisation but is separated chromatographically (Al<sub>2</sub>O<sub>3</sub>) into *mono*-, m.p. 98°, softens at 80°, and *di*-(triphenylmethyl)-xylose, m.p. 100°, softens at 88°,  $[\alpha]_D^{17} + 4.16^\circ$  in C<sub>6</sub>H<sub>6</sub>. Indef. m.p., indistinct cryst. form, and a pronounced tendency to retain solvent make the homogeneity of these compounds very doubtful. Treatment of the crude material with BzCl leads to the isolation of 1:5-di(triphenylmethyl)xylose 2:3-dibenzoate (I), m.p. 235°,  $[\alpha]_D^{17} + 31^\circ$  in C<sub>6</sub>H<sub>6</sub>. Under similar conditions arabinose yields a CPh<sub>3</sub> derivative, m.p. 93°, softens at 86°,  $[\alpha]_D \pm 0^\circ$  in C<sub>6</sub>H<sub>5</sub>N, converted into a diacetate, m.p. 73°, softens at 68°, and a dibenzoate, m.p. 210°. Di(triphenylmethyl)-d-ribose, m.p. 211°, and its diacetate, m.p. 285°, are described. Fructose affords tri(triphenylmethyl)-d-fructose, m.p. 100–112°,  $[\alpha]_D^{15} + 39.7^\circ$  in C<sub>6</sub>H<sub>6</sub> (diacetate, m.p. 97–99°,  $[\alpha]_D^{18} + 28^\circ$  in CHCl<sub>3</sub>). Tri(triphenylmethyl)-l-sorbose diacetate has m.p. 100–103°,  $[\alpha]_D^{18} + 17.2^\circ$  in CHCl<sub>3</sub>. (I) is transformed by HCl-C<sub>6</sub>H<sub>5</sub>N at room temp. into 1-triphenylmethyl-d-xylose 2:3-dibenzoate, m.p. 165°,  $[\alpha]_D^{29} - 4.87^\circ$  in C<sub>6</sub>H<sub>5</sub>N, which with *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>Cl in C<sub>6</sub>H<sub>5</sub>N at room temp. yields the 5-*p*-toluenesulphonate, m.p. 171° diminishing to 165° on exposure to air,  $[\alpha]_D^{19} + 14.4^\circ$  in C<sub>6</sub>H<sub>5</sub>N. Piperidine and arabinose in abs. EtOH at 40° yield piperidine-N-arabinoxide, m.p. 104°,  $[\alpha]_D^{20} - 15.4^\circ$  in C<sub>6</sub>H<sub>5</sub>N, which reverts to its components when exposed to air. The non-cryst. piperidine-N-xyloside is characterised as the very hygroscopic hydrochloride, m.p. 125°,  $[\alpha]_D^{18} + 9.6^\circ$  in EtOH. This is converted by CPh<sub>3</sub>Cl in abs. C<sub>6</sub>H<sub>5</sub>N at room temp. into 1-deoxy-5-triphenylmethyl-1-piperidino-d-xyloketose, m.p. 68°,  $[\alpha]_D^{17} - 4.8^\circ$  in EtOH [hydrochloride (+0.5H<sub>2</sub>O), m.p. 148°,  $[\alpha]_D^{19} - 42.1^\circ$  in EtOH]. H. W.

**Preparation of hexose diphosphate, hexose monophosphate, and phosphoglyceric acid.** K. P. DuBois and V. R. Potter (*J. Biol. Chem.*, 1943, 147, 41–46).—Hexose diphosphate and monophosphate and phosphoglyceric acid are prepared from a single fermenting mixture, and PhMe-treated fresh brewers' yeast is used, instead of the usual Lebedev extract. The rate of formation, and method of isolation, of the P esters from glucose, Na<sub>2</sub>HPO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, and PhMe at pH 7.0 at 37° are examined (cf. Neuberg *et al.*, A., 1943, II, 83). A. T. P.

**Synthesis of 5-D-glucosido-D-arabinose.** N. S. MacDonald and W. L. Evans (*J. Amer. Chem. Soc.*, 1942, 64, 2731–2733).—Gentio-bioseoxime (prep. described), amorphous, with NaOAc-Ac<sub>2</sub>O at 105–120° gives gentiobionitrile octa-acetate (35%), m.p. 108–109°,

$[\alpha]_D^{25} + 8.60^\circ$  in CHCl<sub>3</sub> (with AgNO<sub>3</sub>-MeOH-H<sub>2</sub>O-NH<sub>3</sub> at room temp. gives quantitatively AgCN), converted by NaOMe-MeOH-CHCl<sub>3</sub> at 0°, removal of HCN, and acetylation into 5-D-glucosido-D-arabinose hepta-acetate,  $\beta$ - (I) (32%), m.p. 161–162°,  $[\alpha]_D^{25} - 14.4^\circ$  in CHCl<sub>3</sub>, and  $\alpha$ -form (a little), m.p. 132–133°,  $[\alpha]_D^{25} + 23.1^\circ$  in CHCl<sub>3</sub>. NaOMe-MeOH at 0° hydrolyses (I) to the hygroscopic, amorphous free sugar, which mutarotates to  $[\alpha]_D^{30} - 31.4^\circ$  in H<sub>2</sub>O, reduces Fehling's solution, gives a phenylosazone, m.p. 209–210°, and with NaOMe-MeOH and then boiling dil. HCl gives 100% of pentose (gentiobiose gives none; D-arabinose tetra- and D-glucose penta-acetate give 100%). M.p. are corr. R. S. C.

**Stability of  $\beta$ -methylmaltoside towards hot alkali.** T. J. Schoch, E. J. Wilson, jun., and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, 64, 2871–2872).—The 1:4- $\alpha$ -glucoside linking in  $\beta$ -methylmaltoside and Ca maltobionate and the 1:4- $\beta$ -linking in  $\beta$ -methylcellobioside are stable to hot alkali. Thus, attack on starch by alkali must occur at the terminal CHO (cf. Evans *et al.*, A., 1930, 326). R. S. C.

**Constitution of arabo-galactan. IV. Structure of the repeating unit.** E. V. White (*J. Amer. Chem. Soc.*, 1942, 64, 2838–2842; cf. A., 1942, II, 397).—Arabogalactan (I) and Me<sub>2</sub>SO<sub>4</sub>-30% NaOH-N<sub>2</sub> give a Me ether (OMe 44.4%), which by partial hydrolysis (boiling 0.14N-HCl-MeOH) yields products separated into fractions by light petroleum and Et<sub>2</sub>O. The monosaccharides are investigated by complete methylation and then methanolysis. (I) yields, *inter alia*, 2:3:5-trimethylmethyl-l-arabinoxide, octa- and hepta-methyl-6-d-galactosidogalactose, and a residue containing mainly 2:4-dimethylgalactose anhydride units. The dimethylated units are united more through C<sub>(1)</sub>-C<sub>(6)</sub> than through C<sub>(1)</sub>-C<sub>(3)</sub>, there being also some C<sub>(1)</sub>-C<sub>(3)</sub>-C<sub>(6)</sub> linking. A complete structure is tentatively suggested. R. S. C.

**Polysaccharides of carrageen moss (*Chondrus crispus*). I. Linkage of d-galactose residues and ethereal sulphate.** J. Buchanan, E. E. Percival, and E. G. V. Percival (*J.C.S.*, 1943, 51–54).—The products of methylation and hydrolysis of extracts of carrageen moss by cold and hot H<sub>2</sub>O have been studied. The isolation of  $\beta$ -methylglucoside tetra-acetate, tetramethylglucopyranose, and glucosazone shows that small amounts of glucose are present. Colorimetric determinations on galactose-free syrups indicate ~20% of ketoses. From the isolation of galactosazone, 6-methylgalactosazone, and tetramethyl-d-galactopyranoseanilide, it is inferred that 2-methyl- and 2:6-dimethyl-galactose are present, and that galactose residues constitute 31% of the cold, 33% of the hot, extract. From the slow removal of SO<sub>4</sub> by NaOH and the fact that the OH groups on C<sub>(2)</sub> and C<sub>(6)</sub> are free, it is concluded that the SO<sub>4</sub> residue is attached to C<sub>(4)</sub>, while the galactose residues are joined by positions 1 and 3. A. Li.

**Polysaccharides of Iceland moss (*Cetraria islandica*). I. Hemicelluloses.** H. Granichstaden and E. G. V. Percival (*J.C.S.*, 1943, 54–58).—Hydrolysis of the hemicelluloses extracted from Iceland moss by cold 4% NaOH, after removal of lichenin and lichen acids, yields glucose (89), galactose (8), mannose (3), and a uronic (? glucuronic) acid (5%). Methylation, fractionation, and determinations of  $\eta$  show that the "hemicellulose" is a mixture with mean mol. wt. similar to that of lichenin. Hydrolysis of the fractions produces 2:4:6- (anilide, m.p. 162–166°) and other trimethylglucoses, and shows the presence of galacto- and gluco-pyranose end groups. These results, and investigation of positions 2, 6, and 4 by oxidation and amide formation, production of *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub> derivative, and effect of methanolysis on  $[\alpha]$ , respectively, show that the hemicelluloses consist chiefly of  $\beta$ -glucose units linked through positions 1:2, 1:3, 1:4, and 1:6. A. Li.

**Fractionation of starch by selective precipitation with butanol.** T. J. Schoch (*J. Amer. Chem. Soc.*, 1942, 64, 2957–2961).—Defatted starch (150–450 g.) in H<sub>2</sub>O (1 l.) is added with stirring to boiling H<sub>2</sub>O-BuOH (14:2 l.), autoclaved at 18–20 lb., centrifuged to remove 0.4% of insol. matter, and slowly cooled. The ppt. (~22% for maize or potato starch) is removed by centrifuging (and, if desired, purified by similar reprecipitation); the filtrate yields the sol. portion. The ppt. is spherocryst. (different for maize and potato starches), has a high alkali no., and is more sol. and more liable to gel and retrograde than the sol. part. Other minor differences are also noted. Part of the sol. fraction of maize starch but all that from potato starch undergoes electromigration. The sol. part of potato starch contains all the P, all of which electromigrates. Waxy maize starch gives no insol. fraction. R. S. C.

**Causes of the diversity in acid hydrolysis of starch substances.** M. Samec and M. Dermelj (*Gazzetta*, 1942, 72, 145–150; cf. A., 1930, 416; 1931, 941).—Amylo-amylose (I), the first sol from potato starch heated with H<sub>2</sub>O at 120°, erythro-amylose (II), the sol obtained from later fractions on repeated further heating of the residual gels with H<sub>2</sub>O, and erythro-granulose (III), from Lintner's acid and  $\beta$ -amylase (IV), are hydrolysed (a) by 0.5N- and (b) by 50% H<sub>2</sub>SO<sub>4</sub>. In (a), the reducing power to KMnO<sub>4</sub> increases, at first more rapidly with (II) than with (I), and then vice versa. In (b), the velocity coeff. of (unimol.) hydrolysis of (I) is approx. const up

to 65% decomp., then increases; of (II), increases up to 65% decomp. and then decreases sharply; of (III), increases steadily. This diversity is discussed with reference to the structure of the substances; in (I), fission of  $\alpha$ -1:4 glucosidic linkages precedes that of maltose (more rapid); in (II), mols. with branched linkings, more slowly attacked, accumulate during hydrolysis; in (III),  $\alpha$ -1:4 glucosidic linkages have already been attacked by (IV), and branched linkings are first hydrolysed.

E. W. W.

### III.—HOMOCYCLIC.

**Properties of synthetic lubricating oils. Cyclic hydrocarbons with 22 carbon atoms per molecule.** E. Neyman-Pilat and S. Pilat (*Ind. Eng. Chem.*, 1941, **33**, 1382—1390).—2-Dodecyl-*p*-cymene,  $C_{22}H_{38}$ , b.p. 163—164°/1 mm., and -*p*-menthane,  $C_{22}H_{44}$ , b.p. 159—160°/1 mm.,  $\alpha$ -perhydrocarvacryl- $\beta$ -diisomylethane,  $C_{22}H_{44}$ , b.p. 150—152°/1 mm., and - $\beta$ -(1-decahydronaphthyl)ethane,  $C_{22}H_{40}$ , b.p. 165—166°/1 mm.,  $\alpha\beta$ -dicarvacryl-,  $C_{22}H_{30}$ , b.p. 155—156°/1 mm., and  $\alpha\beta$ -diperhydrocarvacryl-ethane,  $C_{22}H_{42}$ , b.p. 153—154°/1 mm., and 1-dodecyldecahydronaphthalene,  $C_{22}H_{42}$ , b.p. 170—171°/1 mm., are synthesised, and physical consts. are determined. The influence of structure on b.p. is studied. Reduction of the aromatic to the corresponding hydroaromatic rings decreases the b.p. for mono- and di-cyclic uncondensed compounds by 3—4°, and for polycyclic compounds by 50°. Branching of the paraffinic side-chain lowers the b.p. by 7—9°. Splitting the side-chain and alkylation of the rings with shorter chains, and introduction of strongly alkylated rings, e.g., perhydrocarvacryl, lowers the b.p. Introduction of unalkylated rings slightly increases the b.p. for condensed naphthenic rings and uncondensed benzene and cyclohexane rings, and the rise in b.p. is appreciable in the case of condensed polycyclic aromatics. Data obtained by synthesis of pure hydrocarbons may be applied to the determination of the general character of the chemical structure of certain oils.

A. T. P.

**Organic reactions with boron trifluoride. XXVII. Boron trifluoride-catalysed alkylations of halogenobenzenes.** G. F. Hennion and V. R. Pieronek (*J. Amer. Chem. Soc.*, 1942, **64**, 2751—2752; cf. A., 1942, II, 84).—Primary or *sec.* alcohols (Pr, Bu, amyl, octyl; cyclohexanol) with PhCl, PhBr, or PhI,  $BF_3$ , and  $P_2O_5$  (0.25 mol.) at room temp., raised slowly to 75—85°, give 19.1—66.4% of *p*-halogeno-*sec.*-alkylbenzenes. Yields decrease as the mol. wt. of ROH or halogen increases. Absence of *m*-isomerides is proved by oxidation ( $K_2Cr_2O_7$ - $H_2SO_4$ -AcOH at 70—75°) to *p*-Hal- $C_6H_4$ - $CO_2H$  only. The *sec.*-alkyl of the product is proved by conversion of  $C_6H_4Cl$ -CHMeEt by Na in liquid  $NH_3$  at -34° into *p*-CHMeEt- $C_6H_4$ - $NH_2$  (10%) and CHPhMeEt (50%). The following (with *n* and *d*) are recorded:  $\beta$ -*p*-chlorophenyl-propane, b.p. 66—72°/11 mm., -butane, b.p. 81—82°/8 mm., -*n*-pentane, b.p. 93—96°/9 mm., and -*n*-octane, b.p. 106—108°/3 mm.,  $\gamma$ -*p*-chlorophenyl-*n*-pentane, b.p. 95°/10 mm.; *p*-chlorophenylcyclohexane, b.p. 145—147°/19 mm.;  $\beta$ -*p*-bromophenyl-propane, b.p. 58—60°/3 mm., -butane, b.p. 96—98°/8 mm., and -*n*-pentane, b.p. 68—72°/3 mm.;  $\beta$ -*p*-iodophenyl-butane, b.p. 92—94°/3 mm., and -*n*-pentane, b.p. 94—97°/3 mm.

R. S. C.

**Chemical mol. wt. determination of polystyrenes. I.** W. Kern and H. Kammerer (*J. pr. Chem.*, 1942, [ii], **161**, 81—112).—Mol. wt. and Br content of many polystyrenes prepared from styrene and (*p*- $C_6H_4$ Br- $CO$ ) $_2O_2$  in absence or presence of  $Bz_2O_2$  are determined, and constitutions are discussed.

A. T. P.

**Stereoisomeric diphenyloctatetraenes.** L. Zechmeister and A. L. LeRosen (*J. Amer. Chem. Soc.*, 1942, **64**, 2755—2759).—Ph-[CH:CH] $_4$ -Ph (I), m.p. 235—237° (corr.), in boiling  $C_6H_6$  (several hr.), boiling  $Ph_2O$  (15 min.), or  $Ph_2$  at 140° (5 hr.) or with I in  $C_6H_6$  at 25° gives partly two isomerides, separated by chromatography ( $Al_2O_3$ ); irradiation (ultra-violet) in  $C_6H_6$  gives unchanged (I) 83% with 12% and 2%, respectively, of the above-named and traces of two further isomerides. All the isomerides regenerate (I) when kept in  $C_6H_6$  (proved by change of absorption spectra) or rapidly when solutions are evaporated. Steric interference of the *o*- and  $\gamma$ -H greatly decreases the stability of the  $\alpha\beta$ -*cis*-forms. Therefore, (I) is the all *trans* form, the commonest isomerides are *trans-cis-trans-trans* and *trans-cis-cis-trans*, respectively.

R. S. C.

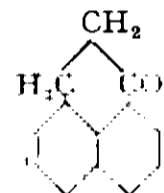
**Arylamine salts as derivatives for identifying aromatic sulphonic acids.** O. C. Dermer and V. H. Dermer (*J. Org. Chem.*, 1942, **7**, 581—586).—The alkali sulphonate, a small excess of freshly distilled amine, HCl, and  $H_2O$  are heated until dissolution is complete, charcoal is added, and the solution is filtered and cooled. The salts are cryst. from 1% AcOH to minimise hydrolysis.  $NH_2Ph$ , *o*- and *p*- $C_6H_4Me$ - $NH_2$  salts of many aromatic sulphonic acids with their m.p. are listed. Some of the m.p. are inconveniently high and blurred by decomp. and the vals. for isomerides and for homologues and other structurally related compounds often do not vary sufficiently to ensure differentiation but the compounds are exceptionally easy to prepare and crystallise and do not show any tendency to form an oil. Almost none are hydrated. The following appear new:  $NH_2Ph$  salt of sulphonic acid of 4-isopropyl-naphthalene-1-

m.p. 190° (decomp.); 2-chlorotoluene-5-, m.p. 229—230.5°; 2-bromotoluene-5-, m.p. 234—236°; *p*-bromobenzene-, m.p. 237—238°; 2-iodotoluene-5-, m.p. 237—239°; 2-chloro-3-nitrotoluene-5-, m.p. 246—248° (decomp.); *p*-*tert*-butylbenzene-, m.p. 249—250°; *p*-ethylbenzene-, m.p. 250—251°; 3:4-dichlorobenzene-, m.p. 254—255°; *p*-phenoxybenzene-, m.p. 256—258°; 4-bromo-3-nitrobenzene-, m.p. 256—259°; 4-*p*-nitrophenoxybenzene-, decomp. 255—260°; 2:4-dinitrobenzene-, m.p. 259—262° (decomp.); 2:5-dichlorobenzene-, m.p. 262—263°; diphenyl-4:4'-di-, m.p. >330° (decomp.). *o*-Toluidine salt of sulphonic acid from: *p*-chlorobenzene-, m.p. 162.5—164°; 3:4-dichlorobenzene-, m.p. 170—172°; 2-chlorotoluene-5-, m.p. 173.5—175°; 2-bromotoluene-5-, m.p. 178—180°; *p*-bromobenzene-, m.p. 182—183.5°; 2-iodotoluene-5-, m.p. 190.5—191.5°; *p*-ethylbenzene-, m.p. 192—193°; 4-bromo-3-nitrobenzene-, m.p. 199—200°; *p*-phenoxybenzene-, m.p. 205.5—207°; *p*-4-nitrophenoxybenzene-, m.p. 226—228°; 2-chloro-3-nitrotoluene-5-, m.p. 235—237° (decomp.); 2:4-dinitrobenzene-, m.p. 245—246.5° (decomp.); 2:5-dichlorobenzene-, m.p. 250—251°; *p*-*tert*-butylbenzene-, m.p. 253—254°; diphenyl-4:4'-di-, m.p. >330° (decomp.). *p*-Toluidine salt of sulphonic acid from: 3:4-dichlorobenzene-, m.p. 204—206°; *p*-ethylbenzene-, m.p. 208—209°; *p*-bromobenzene-, m.p. 215—216.5°; 2-chlorotoluene-5-, m.p. 218—220°; 2-iodotoluene-5-, m.p. 220—222°; 2-bromotoluene-5-, m.p. 222—223°; 4-bromo-3-nitrobenzene-, m.p. 235—236° (decomp.); 2-chloro-5-nitrotoluene-, m.p. 238—240° (decomp.); 2:4-dinitrobenzene-, m.p. 245—247° (decomp.); 2:5-dichlorobenzene-, m.p. 247—248°; diphenyl-4:4'-di-, m.p. >330° (decomp.).

H. W.

**Chloromethylation of naphthalene and the application of 1:5-dichloromethylnaphthalene to the syntheses of polycyclic ring systems. I.** G. Lock and E. Walter (*Ber.*, 1942, **75**, [B], 1158—1163).—Treatment of  $C_{10}H_8$  with paraformaldehyde, AcOH, conc. HCl, and  $H_3PO_4$  gives mainly 1- $C_{10}H_7$ - $CH_2Cl$  (I) with smaller amounts of 1:5- $C_{10}H_6$ ( $CH_2Cl$ ) $_2$  (II), m.p. 150° (corr.), and  $CH_2$ ( $C_{10}H_7$ ) $_2$ . Under similar conditions 1- $C_{10}H_7$ Me yields 48% of 1:4- $C_{10}H_6$ Me- $CH_2Cl$  (III), b.p. 185—189°/17 mm., with viscous material of higher b.p.; if the duration is diminished the yield of (III) falls and unchanged 1- $C_{10}H_7$ Me is left. By diminishing the relative proportion of  $C_{10}H_8$  the yield of (II) can be raised to ~20% but (I) is usually present to the extent of ~20%. (III), KOAc, and boiling AcOH afford 1:5-diacetoxymethylnaphthalene, m.p. 78°, hydrolysed by KOH-aq. EtOH to 1:5-dihydroxymethylnaphthalene, m.p. 127° (bisphenylcarbamate, m.p. 184°). (II) and  $CHNa(CO_2Et)_2$  give *Et* $_2$  di- $\alpha\alpha'$ -carbethoxy- $\beta\beta'$ -1:5-naphthylenedipropionate, m.p. 66.5°, hydrolysed to the tetracarboxylic acid, which is decarboxylated to 1:5-naphthalenedi- $\beta$ -propionic acid, m.p. 258° (corr.). (*Et* $_2$  ester, m.p. 37°). It is converted by HF at room temp. into *Et* perinaphthindan-1-one-7- $\beta$ -propionate (IV), m.p. 90° (semicarbazone, decomp. ~228°).

H. W.

(IV)  $[CH_2]_2 \cdot CO_2H$ 

**Dialkylation of naphthalene. 1:4-Dicyclohexylnaphthalene.** C. C. Price, H. M. Shafer, M. F. Huber, and C. Bernstein (*J. Org. Chem.*, 1942, **7**, 517—521).—The action of  $AlCl_3$  on a mixture of  $Bu^vCl$  and  $C_{10}H_8$  in  $CS_2$  gives a solid mixture of di-*tert*-butylnaphthalenes from which varying proportions of an isomeride (I), m.p. 145—146°, can be separated. This is readily oxidised by  $CrO_3$ -AcOH to a quinone, m.p. 83—83.5° (diacetate, m.p. 139—140°, of the corresponding quinol), but it could not be converted into a picrate. The residue from (I) gives a picrate, m.p. 156—156.5°, from which is obtained a hydrocarbon mixture, m.p. 80—82°, separated by fractional crystallisation from EtOH or AcOH into (I) and an isomeric compound, m.p. 103—104°. Oxidation of these compounds with dil.  $HNO_3$  does not give a naphthalic acid whilst treatment with  $HgSO_4$ - $H_2SO_4$  gives only small amounts of *o*- $C_6H_4$ ( $CO_2O$ ); probably the  $H_2SO_4$  catalyses the elimination of  $Bu^v$  during the oxidation.  $(CH_2 \cdot CO)_2O$  and *p*- $C_6H_4$  $Bu^v_2$  in  $CS_2$  containing  $AlCl_3$  at -15° give almost entirely *p*-*tert*-butylbenzoylpropionic acid, m.p. 126°, identified further by oxidation ( $KMnO_4$ ) to *p*- $C_6H_4$  $Bu^v \cdot CO_2H$ . A small quantity of an ill-defined acid, m.p. 176—177° (benzylthiuronium salt, m.p. 142—143°), also results. The acid is unsaturated towards Br and  $KMnO_4$  and is converted by the latter into compounds, m.p. 194—196° and 217—218°, respectively. The only product which could be obtained under similar conditions from *p*- $C_6H_4$  $Bu^v_2$  and  $(CH \cdot CO)_2O$  is *p*-*tert*-butylbenzoylacrylic acid, plates, m.p. 123°, or needles, m.p. 128°, unsaturated towards Br and oxidised by  $KMnO_4$  to *p*- $C_6H_4$  $Bu^v \cdot CO_2H$ . Passage of  $BF_3$  through a solution of  $C_{10}H_8$  in cyclohexanol at room temp. leads to 1:4-dicyclohexylnaphthalene (II), m.p. 83—83.5°, dehydrogenated by Se at 350° to 1:4- $C_{10}H_6$  $Ph_2$ , m.p. 132—133°. The liquid mixture remaining after removal of (II) is similarly dehydrogenated to  $C_{10}H_6$  $Ph_2$ , m.p. 231°.

H. W.

**Aromatic hydrocarbons and their derivatives. XXXIII. New synthesis of tetracene.** E. Clar (*Ber.*, 1942, **75**, [B], 1271—1273).—Gradual addition of  $AlCl_3$  to tetrahydronaphthalene and *o*- $C_6H_4$ ( $CO$ ) $_2O$  in  $C_2H_2Cl_4$  gives *o*:5:6:7:8-tetrahydro- $\beta$ -naphthoylbenzoic acid, which is immediately dissolved in NaOH and reduced

by Zn dust to *o*-5:6:7:8-tetrahydro- $\beta$ -naphthylmethylbenzoic acid, m.p. 145–147°. It is cyclised by NaCl–ZnCl<sub>2</sub> at 300–310° to 5:12-dihydrotetracene (I), which is dehydrogenated by passage over Cu at 400° or (for small quantities) by chloranil in boiling AcOH to tetracene [2:3-benzanthracene] (II), m.p. 357° (vac.). (I) is best deprived of a yellow colour, due to (II), by heating with a little (CH<sub>3</sub>CO)<sub>2</sub>O in boiling xylene. The absorption spectrum of (I) is essentially that of a simple derivative of C<sub>10</sub>H<sub>8</sub>. H. W.

**Synthesis of polynuclear hydrocarbons from benzanthrone.** N. P. Grechkin and A. E. Arbusov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 50–52).—Benzanthrone and *o*-C<sub>6</sub>H<sub>4</sub>Me·MgBr give 6-*o*-tolyl-benzanthrone, m.p. 150.5–153°, which is pyrolysed to 3:4:6:7-dibenzpyrene, m.p. 238–239°, in 28% yield. Similarly obtained are 6-(2'-methyl-1'-naphthyl)benzanthrone, m.p. 182–184°, and 6:7-benz-3:4-naphthopyrene, m.p. 242–244° (8% yield). F. R. S.

**Alkylation of amines. I.** J. H. Billman, A. Radike, and B. W. Mundy (*J. Amer. Chem. Soc.*, 1942, **64**, 2977–2978).—NH<sub>2</sub>Ph or C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> (3) heated with R<sub>3</sub>PO<sub>4</sub> (R = Me, Et, Pr<sup>a</sup>, or Bu<sup>a</sup>) (2 mols.), followed by boiling 25% NaOH, gives 60–99% of NArAlk<sub>2</sub>. Pr<sup>β</sup><sub>3</sub>PO<sub>4</sub> gives 80.5% of NHPPhPr<sup>β</sup>. *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub> decomposes under the conditions of alkylation. R. S. C.

**cyclobutane derivatives. I. Degradation of cis- and trans-cyclobutane-1:2-dicarboxylic acids to the corresponding diamines.** E. R. Buchman, A. O. Reims, T. Skei, and M. J. Schlatter. **II. Thermal decomposition of trans-cyclobutane-1:2-bis(trimethylammonium) hydroxide.** E. R. Buchman, M. J. Schlatter, and A. O. Reims (*J. Amer. Chem. Soc.*, 1942, **64**, 2696–2700, 2701–2703).—I. (CH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub> at 70–80° with SOCl<sub>2</sub> and then Br (later at 100°) and finally MeOH at 0° gives *meso*- (I) (70%), m.p. 73.5–74° and *dl*-(CH<sub>2</sub>·CHBr·CO<sub>2</sub>Me) (II) (~20%), m.p. 11–12°. With boiling KCN–MeOH, (I) and (II) give comparable yields (~72%) of Me<sub>2</sub> 1-cyanocyclobutane-1:2-dicarboxylates, m.p. 89.5–90° (III) (~28%), and b.p. 119–120°/2 mm. (IV) (~72%); a compound, C<sub>10</sub>H<sub>12</sub>O<sub>5</sub>N<sub>2</sub> (? related to Me<sub>2</sub> *aa'*-dicyanoadipate), m.p. 172.5–173.5° (decomp.), is also isolable from old specimens. Hydrolysis (Fuson *et al.*, A., 1929, 794; 1934, 1104) of (III) gives cyclobutane-1:1:2-tricarboxylic acid, m.p. (+xH<sub>2</sub>O) 135° (decomp.) or (anhyd.) 91–92° (loses CO<sub>2</sub> at ~130°). Hydrolysis of crude (IV) by boiling 6N-HCl, decarboxylation at 170–180°/20 mm., boiling with AcCl, and final distillation gives 81% of *cis*-cyclobutane-1:2-dicarboxylic anhydride, m.p. 76.5–77°, b.p. 127–130°/2 mm., and thence (boiling H<sub>2</sub>O) the *cis*-acid (V) (85%), m.p. 139.5–140°, which at 200° gives 51% of *trans*-acid (VI), m.p. 130.5–131°. With CH<sub>2</sub>N<sub>2</sub>, (V) gives 94% of *cis*-Me<sub>2</sub> ester (VII), b.p. 85°/3 mm., and with boiling HCl–EtOH gives 71% of *cis*-Et<sub>2</sub> ester, b.p. 99–100°/2 mm. Hydrolysis, decarboxylation, and esterification of crude (IV) gives 82% of mixed Et<sub>2</sub> esters. (VII) is largely isomerised by boiling MeOH–NaOMe; hydrolysis then gives 76% of (VI). N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O at 130° converts the esters into *cis*-, *forms*, m.p. (stable) 140–140.5° and 134.5–135°, and *trans*-cyclobutane-1:2-dicarboxyldihydrazide, m.p. 223–223.5°, the latter being readily obtained from the mixed esters and both yielding by hydrolysis their respective acids. Treating the derived *dihydrochlorides* [trans-, m.p. ~200° (decomp.)], with NaNO<sub>2</sub>–H<sub>2</sub>O–Et<sub>2</sub>O at 13–16°, evaporating the Et<sub>2</sub>O layer diluted with EtOH, and boiling the resultant EtOH solution gives *cis*-, m.p. 101.5–102° [and a little (?) 4:5-dimethylenedihydrouacil, m.p. 258.5–259°], and *trans*-NN'-dicarbethoxy-1:2-diaminocyclobutane, m.p. 129.5–130°, which, when boiled with KOH–MeOH and distilled at 170° in steam, give respectively *cis*- (VIII) (77%), b.p. 147°/760 mm., 75°/50 mm., and *trans*-1:2-diaminocyclobutane (IX) (63%), b.p. 151°/760 mm., 74°/50 mm. [*cis*-, sublimes ~150° (decomp.), and *trans*-carbonate, sublimes ~110° (decomp.)]; *cis*-, m.p. 145.5–146.5°, and *trans*-(PhSO<sub>2</sub>)<sub>2</sub>, m.p. 153.5–154°, and *cis*-, m.p. 204.5–205°, and *trans*-Bz<sub>2</sub> derivative, m.p. 245.5–246°; *cis*-, m.p. 255° (decomp.), and *trans*-dipicrate, m.p. 254° (decomp.); *trans*-bis-phenylcarbamyl derivative, m.p. 279–280°; *trans*-oxalate, m.p. 268° (decomp.)]. (VIII) and (IX) are also obtained from (V) and (VI) respectively by, successively, H<sub>2</sub>SO<sub>4</sub>–CHCl<sub>3</sub>–N<sub>3</sub>H at 40°, aq. KOH, and steam-distillation at ~160°. Bz<sub>2</sub> with (VIII) or (IX) gives tetraphenylpyrazine. With COCl<sub>2</sub>–Et<sub>2</sub>O at 0°, (VIII) gives the cyclic carbamide, m.p. 147–147.5°, but (IX) gives an amorphous substance. With CS<sub>2</sub>–EtOH, (VIII) gives a dithiocarbamate, which sinters at ~152° giving H<sub>2</sub>S and 2-thiol-4:5-dimethylene-4:5-dihydroglyoxaline, m.p. 168.5–169°, formed also by evaporating an aq. solution of the salt. (IX) gives a dithiocarbamate, C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>S<sub>2</sub>, sinters at 263°. MeCS·NH<sub>2</sub> and (VIII) give exothermally (later at 80°) 2-methyl-4:5-dimethylene-4:5-dihydroglyoxaline, m.p. 89–90° (picrate, m.p. 150–150.5°); (IX) reacts after heating to give a substance whence it is readily regenerated by hydrolysis.

**II.** The crude dihydrochloride of (IX) with boiling 90% HCO<sub>2</sub>H–36% CH<sub>2</sub>O gives *trans*-1:2-bisdimethylaminocyclobutane (X), b.p. 83°/50 mm. [dipicrate, m.p. 244° (decomp.)] [(VIII) gives a tar], but with boiling MeI–KOH–MeOH gives 2-dimethylaminocyclobutyltrimethylammonium iodide, decomp. 218–218.5°, which with MeI–EtOH at 100° gives (XI). The dimethiodide (XI), m.p. 251° (decomp.) [corresponding dipicrate, m.p. 288° (decomp.)], of (X) with Ag<sub>2</sub>O–H<sub>2</sub>O gives the dimethoxyhydroxide, which at ~250° or

with Pt–asbestos at 350–360° gives cyclobutanone, b.p. 98.5–99° [semicarbazone, m.p. 212–212.5°; phenylhydrazone, m.p. 98–98.5°; 2:4-dinitrophenylhydrazone, m.p. 147–147.2° (lit. 132–133°)], 2-1'-hydroxy-1'-cyclobutyl- and 2-cyclobutylidene-cyclobutanone, separated by chromatography of the 2:4-dinitrophenylhydrazones, orange, m.p. 186–187° (decomp.), and red, sinters at 184° (decomp.), respectively, 1:5 NHMe<sub>2</sub>–NMe<sub>3</sub>, and (X). 1-Dimethylamino- $\Delta^1$ -cyclobutene is postulated as an unstable intermediate. M.p. are corr. R. S. C.

**Acetoacetaryl amides.**—See B., 1943, II, 108.

**N-Polyhydroxyalkylarylamines.**—See B., 1943, II, 107.

**Derivatives of N-phenylarylamines.**—See B., 1943, II, 107.

**5-Acetamididosaccharin, a derivative of sulphanilamide.** O. G. Backeberg and J. L. C. Marais (*J.C.S.*, 1943, 78–79).—*m*-C<sub>6</sub>H<sub>4</sub>Me·NHAc and ClSO<sub>3</sub>H at 0° give 3:1:6-NHAc·C<sub>6</sub>H<sub>3</sub>Me·SO<sub>2</sub>Cl (I), converted into *acet-m-toluidide-6-sulphonamide* (II), m.p. 204°, and -6-sulphonanilide, m.p. 155°. (II) and Br–AcOH or aq. NaOH–NaOBr give the 4(?)–Br-derivative, m.p. 262°, hydrolysed (boiling 10% aq. NaOH) to 4(?)–bromo-*m*-toluidine-6-sulphonamide, m.p. 185°. (I) or (II) and boiling 10% aq. NaOH afford 3:1:6-NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me·SO<sub>3</sub>H (with Br–H<sub>2</sub>O gives 1:2:4:6:3-C<sub>6</sub>HMeBr<sub>3</sub>·NH<sub>2</sub>) or *m*-toluidine-6-sulphonamide (III), m.p. 172° [2:4(?)–Br<sub>2</sub>-derivative, m.p. 198°; Bz<sub>2</sub> derivative, m.p. 265°, also prepared from *m*-C<sub>6</sub>H<sub>4</sub>Me·NHBz and ClSO<sub>3</sub>H, followed by NH<sub>3</sub>], respectively. 6:1:3-NH<sub>2</sub>·SO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me·N<sub>2</sub>HSO<sub>4</sub> [from (III) and H<sub>2</sub>SO<sub>4</sub>–OMe·NO–MeOH] with boiling H<sub>2</sub>O gives *m*-cresol-6-sulphonamide, m.p. 207°, methylated by Me<sub>2</sub>SO<sub>4</sub>–aq. NaOH to 3:1:6-OMe·C<sub>6</sub>H<sub>3</sub>Me·SO<sub>2</sub>·NH<sub>2</sub>. (II) and aq. KMnO<sub>4</sub> at 85° give 5-acetamididosaccharin, m.p. 299°, but attempted deacetylation gives a non-cryst. syrup. A. T. P.

**Sulphanilamide derivatives. VIII. Sulphanilylamidines.** E. H. Northey, A. E. Pierce, and D. J. Kertesz (*J. Amer. Chem. Soc.*, 1942, **64**, 2763–2765; cf. A., 1940, II, 304).—NH<sub>2</sub>·CMe·NH<sub>2</sub>·HCl, *p*-NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Cl, and 50% NaOH in COMe<sub>2</sub> at 10–20° give N<sup>4</sup>-acetylsulphanilylacetylamidine, m.p. 244.2–244.7°, hydrolysed by 7.5N-HCl at 60° to *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH<sub>2</sub> (I). Sulphanilyl-acet- (II), m.p. 151.4–152° (lit. 149°), -isohexo-, m.p. 126–127.2°, - $\alpha$ -phenyl-acet-, m.p. 177–179°, -benz-, m.p. 210.2–210.7° (lit. 203°), and -*p*-tolu-amidine, m.p. 234.9–235.4°, are prepared from NH<sub>2</sub>·CR·NH<sub>2</sub>·HCl by NaOH–*p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Cl (III)–COMe<sub>2</sub>, followed by Fe dust in dil. HCl at 95–100°, the intermediate NO<sub>2</sub>-compounds having m.p. 190.7–191.3°, 247–250° (decomp.), 194.3–195.8°, 180.3–181°, and 149.5–160°, respectively. Disubstitution also occurs in amounts varying with the amount of (III) used; disulphanilyl-acet-, m.p. 191.6–191.8°, -benz-, m.p. 206.4–207.6° (decomp.), and -*p*-tolu-amidine, m.p. 166.9–167.5°, and the corresponding (NO<sub>2</sub>)<sub>2</sub>-compounds, m.p. 189–190.7°, 241.8–242.6°, and 213.7–214.9°, respectively, sol. in alkali, are described. N<sup>1</sup>-Nicotinoyl-*p*-nitrobenzenesulphonamide and PCl<sub>5</sub> in POCl<sub>3</sub> at 80–85° give the imide chloride, which with aq. NH<sub>3</sub> gives *p*-nitrobenzenesulphonyl-, m.p. 232.5–233.5°, and thence *p*-sulphanilyl-nicotinamidide, m.p. 208.1–208.2°. *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·N·CPhCl with aq. NH<sub>2</sub>Me, NH<sub>2</sub>Et, or 2-aminopyridine–COMe<sub>2</sub> gives similarly N-*p*-nitrobenzenesulphonyl-N'-methyl-, m.p. 181.2° (decomp.), and -N'-2'-pyridyl-benzamidide, m.p. 180.7° (decomp.), and N-*p*-sulphanilyl-N'-methyl-, m.p. 228.1–229.2°, -N'-N'-diethyl-, m.p. 193.7–194°, and -N'-2'-pyridyl-benzamidide, m.p. 206.8–207.5°. The sulphanilylamidines are ArSO<sub>2</sub>·N·CR·NH<sub>2</sub> [since acid or alkaline hydrolysis yields (I)] and probably ArSO<sub>2</sub>·N·CR·NH·SO<sub>2</sub>Ar etc. The physiological activity of (II) is equal to that of (I), but that of the other sulphanilylamidines is low. M.p. are corr. R. S. C.

***p*-Aminobenzenesulphonylguanidylguanidine and derivatives.**—See B., 1943, III, 88.

***p*-cyclo-Hexylaminodiphenylamine.**—See B., 1943, II, 107.

**Nitrophenylallylthiosemicarbazides. Analytical properties.** A. W. Scott and J. T. Andrews (*J. Amer. Chem. Soc.*, 1942, **64**, 2873–2874).—CH<sub>2</sub>·CH·CH<sub>2</sub>·NH·CS·NH·NHPh (I) and its *o*-, *m*-, m.p. 120°, and *p*-NO<sub>2</sub>-derivative (II), m.p. 188° (decomp.), give colours or ppts. with Ag, Hg<sup>I</sup>, Hg<sup>II</sup>, and Cu<sup>II</sup>. The sensitivity is *p* >> *o* > *m*-NO<sub>2</sub>, (I). (II) gives a ppt. with solutions containing 1 p.p.m. of Hg<sup>II</sup> and a slight colour with 1 pt. in 10<sup>2</sup>; unsatisfactory quant. results were obtained. R. S. C.

**Reversible photochemical processes in rigid media. Dissociation of organic molecules into radicals and ions.**—See A., 1943, I, 133.

**Initial step in the action of acids on tetra-arylhydrazines.** G. N. Lewis and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1942, **64**, 2808–2810).—Addition of HCl to (NPh<sub>2</sub>)<sub>2</sub> causes initial formation, even near liquid air temp., of NPh<sub>2</sub><sup>+</sup>, spectroscopically identified. Both NPh<sub>2</sub>Cl and NPh<sub>2</sub><sup>+</sup> are too unstable to be observed except at very low temp. W. R. A.

**5-tert.-Amyl-*o*-cresol.**—See B., 1943, II, 107.

**Long-chain acyl- and alkyl-phenols.** K. Paranjpe, N. L. Phalnikar, and K. S. Nargund (*J. Univ. Bombay*, 1942, **11**, A, Part 3, 120–123).—PhOH, RCO<sub>2</sub>H, and ZnCl<sub>2</sub> yield >70% of *o*-OH·C<sub>6</sub>H<sub>4</sub> undecyl, tridecyl, pentadecyl, new m.p. 58°, and heptadecyl ketone.

*new* m.p. 66—67°. *Me ethers*, b.p. 110°/50 mm., 180—182°/66 mm., and 180—182°/66 mm. (m.p. 38°), and m.p. 42° (oxidised by  $\text{KMnO}_4$  in  $\text{COMe}_2$  to  $\text{o-OMe-C}_6\text{H}_4\text{-CO}_2\text{H}$ ), respectively], reduced (Clemmensen) to *o-hydroxydodecyl*, b.p. 175°/30 mm., *tetradecyl*, b.p. 170°/60 mm., *hexadecyl*, b.p. 210°/45 mm., and *octadecyl-benzene*, m.p. 58°, respectively.  $\text{PhOMe}$ ,  $\text{RCOCl}$ , and  $\text{AlCl}_3$  in  $\text{PhNO}_2$  yield >84% of  $\text{p-OMe-C}_6\text{H}_4$  *undecyl*, m.p. 57° (oxime, m.p. 60°), *tridecyl*, m.p. 63° (semicarbazone, m.p. 71°; oxime, m.p. 66°), *pentadecyl*, and *heptadecyl ketone*, m.p. 75° (oxidised to  $\text{p-OMe-C}_6\text{H}_4\text{-CO}_2\text{H}$ ). These are demethylated to the phenols, and reduced (Clemmensen) to *p-methoxy-dodecyl*, b.p. 180°/50 mm., *tetradecyl*, b.p. 210°/60 mm., *hexadecyl*, m.p. 54°, and *octadecyl-benzene*, m.p. 60°, respectively.

A. Li.

*p-Toluenesulphonates of nitro-4-phenylphenols*. S. E. Hazlet, D. A. Stauffer, and H. O. Van Orden (*J. Amer. Chem. Soc.*, 1942, 64, 3057).—2 : 6-Di-, m.p. 186—187°, and 2 : 6 : 4'-tri-nitro-4-diphenyl *p-toluenesulphonate*, m.p. 219—220°, are prepared from the appropriate  $\text{NO}_2$ -phenol and  $\text{p-C}_6\text{H}_4\text{Me-SO}_2\text{Cl}$  in  $\text{C}_2\text{H}_5\text{N}$  or  $\text{C}_5\text{H}_5\text{N}$ -dioxan, respectively.

R. S. C.

Structure of Skita's "9 : 10-dihydroxydecahydrophenanthrene." P. Levine (*J. Amer. Chem. Soc.*, 1942, 64, 3046—3047).—Skita's so-called 9 : 10-dihydroxy-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10-deca- (A., 1926, 173; cf. A., 1943, II, 65) is 9 : 10-dihydroxy-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octa-hydrophenanthrene (I), since it consumes 1 equiv. of  $\text{Pb}(\text{OAc})_4$  in  $\text{C}_6\text{H}_6$  to give the quinone, which with Zn dust and a trace of  $\text{NEt}_3$  in  $\text{Ac}_2\text{O}$  gives the diacetate of (I).

R. S. C.

Phenylethylamines. IV. Dimethoxy- and dihydroxy-phenyl-n-propylamines. E. H. Woodruff (*J. Amer. Chem. Soc.*, 1942, 64, 2859—2862; cf. A., 1940, II, 213).—Hydrolysis and methylation of hydroxy-4-methylcoumarins gives *trans*-( $\text{OMe}$ ) $_2\text{C}_6\text{H}_3\text{-CMe-CH-CO}_2\text{H}$ . ( $\text{OMe}$ ) $_2\text{C}_6\text{H}_3\text{-COMe}$  gives by the Reformatsky reaction and dehydration at 250—300° etc. 2 : 3-, m.p. 121—122° (Et ester, b.p. 165—175°/8 mm.), 2 : 6-, m.p. 143—144° (*form*, m.p. 185—185.5°, obtained from 6-hydroxy-4-methylcoumarin) (Et ester, b.p. 136—138°/0.03 mm.), 3 : 4-, m.p. 138—140° (Et ester, b.p. 200—203°/11 mm.), and 3 : 5-dimethoxy- $\beta$ -methylcinnamic acid, m.p. 123.5—124.5° (Et ester, b.p. 197—203°/11 mm.). Electrolytic reduction of cinnamic acids gives  $\beta$ -2 : 3-, m.p. 77°, b.p. 181—184°/0.15 mm., -2 : 4-, m.p. 104—105°, -2 : 5-, m.p. 78—79°, b.p. 175—185°/0.1 mm., -2 : 6-, m.p. 78.5—79°, b.p. 190—197°/3 mm., -3 : 4-, m.p. 84—85°, and -3 : 5-dimethoxyphenyl-n-butyric acid, b.p. 184—185°/0.05 mm., and thence the amides, m.p. 90—91°, 133—134°, 122° (lit. 121°), 153—155°, 131°, and 92.5—93°, respectively, which with  $\text{NaOBr}$  give  $\beta$ -2 : 3-, b.p. 150—154°/11 mm. (133.5—134°),  $\beta$ -2 : 4-, b.p. 158—160°/14 mm. (146—147°),  $\beta$ -2 : 5-, b.p. 164—166°/16 mm. (149—150°),  $\beta$ -2 : 6-, b.p. 155—158°/5 mm. (143—145°),  $\beta$ -3 : 4-, b.p. 163—166°/15 mm. (205—206°), and  $\beta$ -3 : 5-dimethoxyphenyl-n-propylamine, b.p. 179—184°/14 mm. (105—107°), figures in parentheses being m.p. of the hydrochlorides. Conc.  $\text{HCl}$  at 160° then yields the corresponding  $\beta$ -dihydroxyphenyl-n-propylamine hydrochlorides, m.p. 191—191.5°, 222—223°, 167.5—169.5°, 93—95°, 180—181°, and 164—166°, respectively. 5-Hydroxy-4-methylcoumarin and  $\text{H}_2$ -Raney Ni in  $\text{EtOH}$  at 60°/60 lb. give 5-hydroxy-4-methyl-3 : 4-dihydrocoumarin, m.p. 160°, b.p. 214°/5 mm.

R. S. C.

3-Alkoxydiphenyls. See B., 1943, II, 108.

Rôle of neighbouring groups in replacement reactions.—See A., 1943, II, 117.

4-Nitrodiphenyl ether-4'-sulphonyl chloride and -4'-sulphonamide. V. H. Dermer and O. C. Dermer (*J. Amer. Chem. Soc.*, 1942, 64, 3056—3057).— $\text{p-NO}_2\text{-C}_6\text{H}_4\text{-OPh}$  and warm conc.  $\text{H}_2\text{SO}_4$  give 4- $\text{NO}_2\text{-C}_6\text{H}_4\text{-O-C}_6\text{H}_4\text{-SO}_2\text{H}$  (I), converted by  $\text{PCl}_5$  into 4-nitrodiphenyl ether-4'-sulphonyl chloride, m.p. 84—85° (corr.), which is also obtained (m.p. 85.5—86.5°) from  $\text{p-OPh-C}_6\text{H}_4\text{-SO}_2\text{Cl}$  by  $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-AcOH}$  at 60—70° and yields the amide, m.p. 130—131°. The acid of Jones *et al.* (A., 1916, i, 644) was (I).

R. S. C.

$\alpha\alpha\beta$ -Tri-*p*-anisyl- $\Delta^1$ -propene and -butene.—See B., 1943, III, 88.

Attempted asymmetric syntheses involving the Grignard reagent in optically active solvents. D. S. Tarbell and M. C. Paulson (*J. Amer. Chem. Soc.*, 1942, 64, 2842—2844).— $\text{CHPhMe-OH}$  is inactive when prepared from  $\text{MgMeI}$  and  $\text{PhCHO}$  in  $d\text{-CHMeEt-OMe}$  or bornyl-dimethylamine (I), but in (I) a dextrorotatory by-product is formed. In *l*-menthyl  $\text{Me ether}$  (II), b.p. 83°/12 mm.,  $[\alpha]_D^{25}$  -95.6°,  $\text{MeI}$  or  $\text{EtI}$  with  $\text{Mg}$  gives an insol. product preventing further reaction;  $\text{MgMeI}$  ( $\text{Et}_2\text{O}$  removed after prep.) and  $\text{Pr}^n\text{CHO}$  in (II) give  $\text{Bu}^n\text{OH}$  and  $\text{COMePr}^n$ . Heating  $\text{Mg}$  and  $\text{PhBr}$  in (I) at 130—140° and then adding paraldehyde at 110—120° gives  $\text{CHPhMe-OH}$  (45—60%),  $\alpha$  usually 0.

R. S. C.

Phenol-formaldehyde resins. Acetylation of hydroxybenzyl alcohols. R. Barthel (*J. pr. Chem.*, 1942, [ii], 161, 77—80).— $\text{o-OH-C}_6\text{H}_4\text{-CH}_2\text{-OH}$ ,  $\text{PhOH}$ , and  $\text{Ac}_2\text{O}$  give  $\text{PhOAc}$  and *o-acetoxybenzyl acetate*, b.p. 103—104°/1 mm. 1 : 4 : 2 : 6- $\text{OH-C}_6\text{H}_3\text{Me}(\text{CH}_2\text{-OH})_2$  similarly affords its triacetate, b.p. 157—158°/1 mm. Acetylation ( $\text{Ac}_2\text{O}$ ) of the resin obtained when 1 : 4 : 2- $\text{OH-C}_6\text{H}_3\text{Me-CH}_2\text{-OH}$  is heated at 150° for a short time gives little of the corresponding

diacetate, b.p. 122—123°/1 mm., and a product hydrolysed to di-2-hydroxy-5-methylbenzyl ether, m.p. 101—102°.

A. T. P.

Formation of phenol-formaldehyde resins. X. Mechanism of "hardening" of resols. "Hardening" of *p*-hydroxymesityl alcohol. E. Adler, H. von Euler, and J. O. Cedwall (*Arkiv Kemi, Min., Geol.*, 1942, 15, A. No. 7, 17 pp.; cf. B., 1942, II, 25).—4 : 3 : 5 : 1- $\text{OH-C}_6\text{H}_3\text{Me}_2\text{-CH}_2\text{-OH}$  (I) (from 2 : 6 : 1- $\text{C}_6\text{H}_3\text{Me}_2\text{-OH}$  and 40%  $\text{CH}_2\text{O}$  in 5%  $\text{NaOH}$  for 24 hr.) at 140—155° for 30—60 min. gives 55—57% of unchanged (I),  $\text{CH}_2\text{O}$ , 10—13% of (4 : 3 : 5 : 1- $\text{OH-C}_6\text{H}_3\text{Me}_2$ ) $_2\text{CH}_2$ , 1—15% of di-(4-hydroxy-3 : 5-dimethylbenzyl) ether, m.p. not given, and 0—5% of 4 : 4'-dihydroxy-3 : 5 : 3' : 5'-tetramethyl- $\alpha\beta$ -diphenylethane (II, m.p. 168—169° [diacetate, m.p. 148—149°;  $\text{Me}_2$ , m.p. 88—88.5°, insol. in dil.  $\text{NaOH}$ , and  $\text{Me}_2$  ether, m.p. 108—109°]). At 170—180° (I) gives in good yield (II) and 4 : 4'-dihydroxy-3 : 5 : 3' : 5'-tetramethylstilbene (III), m.p. 233—236° [diacetate, m.p. 239—240°, gives a red colour with  $\text{C}(\text{NO}_2)_4$ ], separated via the insol. (II)- $\text{C}_5\text{H}_5\text{N}$  complex. (III) is reduced to (II) by  $\text{H}_2$ - $\text{PtO}_2$  in  $\text{AcOH}$ , but not in  $\text{EtOAc}$ , and gives with  $\text{Br-Et}_2\text{O}$  the dibromide, m.p. 187° (decomp.), and thence (KOH) (4 : 3 : 5 : 1- $\text{O-C}_6\text{H}_3\text{Me}_2\text{-CH}_2$ ) $_2$ . It is concluded that condensation in  $\text{PhOH-CH}_2\text{O}$  type resins at low temp. takes place by way of  $\text{-CH}_2\text{-O-CH}_2\text{-}$  and  $\text{-CH}_2\text{-}$  linkings, which are supplemented at high temp. by  $\text{-CH}_2\text{-CH}_2\text{-}$  and  $\text{-CH-CH-}$  linkings formed from *p*-quinonemethides. At all temp. condensation occurs primarily *para* to  $\text{OH}$ , followed by secondary cross-linkings in the *o*-positions.

M. H. M. A.

$\alpha\alpha\beta\beta$ -Tetraphenylethanol. A. Banchetti (*Gazzetta*, 1942, 72, 74—77; cf. Wegler, A., 1934, 292).—The best prep. of  $\text{CHPh}_2\text{-CPh}_2\text{-OH}$  (I) is that of Paternò *et al.* (A., 1909, i, 393). When distilled at atm. pressure, (I) gives  $(\text{CHPh}_2)_2$  (II), which may account for the variability of m.p. assigned to (I). Using the Kofler microscope, m.p. of (I) and (II) are 244° and 215°, respectively.

E. W. W.

Reaction of magnesium *n*-butyl bromide with aromatic ketones. (Misses) H. M. Crawford, M. E. Saeger, and F. E. Warneke (*J. Amer. Chem. Soc.*, 1942, 64, 2862—2864).— $\text{MgBu}^n\text{Br}$  (I) with  $\text{COPhMe}$  gives  $\beta$ -phenyl-n-hexan- $\beta$ -ol (72—80%), b.p. 123—124°/9 mm., dehydrated by Lucas reagent to  $\beta$ -phenyl- $\Delta^1$ -n-hexene, b.p. 223—226°.  $\text{COPh}_2$  and (I) give  $\text{CHPh}_2\text{-OH}$  (17—30%) and  $(\text{CHPh}_2)_2\text{O}$  (5—6%).  $\text{Bz}_2$  and (I) give benzoin (0—13%).  $\alpha\beta$ -diphenyl-n-hexan- $\beta$ -ol- $\alpha$ -one (II) (0.5—5.6%), m.p. 124°, and  $\epsilon\zeta$ -diphenyl-n-decane- $\epsilon\zeta$ -diol (0—trace), m.p. 184°. Dehydration (Lucas reagent) of (II) gives  $\alpha\beta$ -diphenyl- $\Delta^1$ -n-hexen- $\alpha$ -one, b.p. 288—290°.  $\text{COPh-CH}_2\text{Ph}$  gives 0—7.4% of  $(\text{CHPh})_2$ , 0—traces of  $[\text{CH}_2\text{Ph-CPh}(\text{OH})]_2$ , and 0—traces of the ? pinacolone, m.p. 133°.

R. S. C.

Action of alkaline reagents on  $\alpha\delta$ -dihalogeno- $\alpha\delta$ -dibenzoylbutanes. R. C. Fuson, H. H. Hully, J. F. McPherson, and F. W. Spangler (*J. Org. Chem.*, 1942, 7, 462—465; cf. A., 1932, 746; 1940, II, 178).— $\alpha\delta$ -Dibromo- $\alpha\delta$ -dibenzoylbutane is converted by alkaline reagents, best  $\text{NH}_4\text{Et}$ , into 5-bromo-5-benzoyl-1-phenyl- $\Delta^1$ -cyclopentene oxide (I), m.p. 138—139°, converted by  $\text{NH}_2\text{OH}$  into an oxime (II), m.p. 178—179° (decomp.), and an unstable compound, m.p. 90—93° (decomp.). (II) and  $\text{SOCl}_2$  in  $\text{CHCl}_3$  give the corresponding 5-carboxyanilide, m.p. 172—173° (decomp.).  $\text{MgPhBr}$  and (I) in  $\text{Et}_2\text{O}$  afford 5-bromo-1-phenyl-5- $\alpha$ -hydroxybenzhydryl- $\Delta^1$ -cyclopentene oxide, m.p. 127—129° (decomp.), converted by Zn dust in boiling  $\text{AcOH}$  into (probably) 1-phenyl-5-benzhydrylidene- $\Delta^1$ -cyclopentene oxide, m.p. 159—160°. ( $\text{Bz-CH}_2$ ) $_2$  and  $\text{Cl}_2$  in hot  $\text{CCl}_4$  give  $\alpha\delta$ -dichloro- $\alpha\delta$ -dibenzoylbutane, m.p. 177—178°, transformed by  $\text{NH}_4\text{Et}$  in boiling  $\text{C}_6\text{H}_6$  into 5-chloro-5-benzoyl-1-phenyl- $\Delta^1$ -cyclopentene oxide (III), m.p. 131—132° (oxime, m.p. 168—169°), which does not give a ppt. with boiling  $\text{AgNO}_3\text{-EtOH}$  and does not decolorise  $\text{KMnO}_4$  in  $\text{COMe}_2$ . (III) is reduced by Zn and  $\text{AcOH}$  to ( $\text{Bz-CH}_2$ ) $_2$ . With  $\text{MgPhBr}$  in  $\text{Et}_2\text{O}$  (III) yields 5-chloro-1-phenyl-5- $\alpha$ -hydroxybenzhydryl- $\Delta^1$ -cyclopentene oxide (IV), m.p. 169.5—170.5°, which is rearranged by  $\text{HCl}$  in  $\text{Et}_2\text{O}$  to a compound,  $\text{C}_{24}\text{H}_{21}\text{O}_2\text{Cl}$ , m.p. 70—80°. Reduction of (IV) by Zn dust and boiling  $\text{AcOH}$  gives 1-phenyl-5- $\alpha$ -hydroxybenzhydryl- $\Delta^1$ -cyclopentene oxide, m.p. 112—113°. H. W.

Autoxidation of hydrocarbons. VI. Indane peroxide. H. Hock and S. Lang (*Ber.*, 1942, 75, [B], 1051—1054).—Freshly distilled indane is treated with dry  $\text{O}_2$  while irradiated at 60°, the product is treated with 25%  $\text{NaOH}$  at -5°, and the resulting Na salts are acidified and extracted with  $\text{Et}_2\text{O}$ ; the  $\text{Et}_2\text{O}$  solution is washed with aq.  $\text{NaHCO}_3$  (the acid removed contains a little homophthalic acid) dried, and distilled, thus giving 1-indanyl *H* peroxide (I), b.p. 64—65°/0.01 mm., 74—75°/0.04 mm., violent decomp. 135—140°. (I) is catalytically decomposed by aq.  $\text{FeSO}_4$  at 100° into indan-1-one (II) (70%), obtained also in 90% yield by the oxidation of (I) by  $\text{Pb}(\text{OAc})_4$  in  $\text{AcOH}$  at 15—25°. Reduction of (I) by  $\text{Na}_2\text{SO}_3\text{-H}_2\text{O}$  affords indan-1-ol (III), new m.p. 39°. Decomp. of (I) with 2*N*- $\text{NaOH}$  at 70° affords (II) and (III). (I) and  $\text{Me}_2\text{SO}_4$  give 1-indanyl *Me* peroxide, b.p. 43—44°/0.05 mm., vigorous decomp. 140°. H. W.

Characteristics of  $\beta$ -hydroxy- $\beta$ -2 : 5-dimethoxyphenylisopropylamine hydrochloride. R. Baltzly and J. S. Buck (*J. Amer. Chem. Soc.*, 1942, 64, 3040).—The substance, m.p. 176° (decomp.), previously (A., 1940, II, 83) thus named is  $\alpha$ -2 : 5-dimethoxybenzoyl-ethylamine hydrochloride and is hydrogenated ( $\text{Pt-black}$ ;  $\text{H}_2\text{O}$ ) to

$\beta$ -hydroxy- $\beta$ -2 : 5-dimethoxyphenylisopropylamine (hydrochloride, m.p. 215°;  $Ac_2$  derivative, m.p. 120°). R. S. C.

**Hydrogenated acids of chaulmoogra oil.** N. P. Buu-Hoi and P. Cagniant (*Ber.*, 1943, 75, [B], 1181—1189).—Catalytic hydrogenation (Raney Ni) of Ethydnocarpate, b.p. 158—161°/0.2 mm.,  $[\alpha]_D^{25} \sim +56^\circ$ , and Et chaulmoograte, b.p. 171—172°/0.2 mm.,  $[\alpha]_D^{25} \sim +51^\circ$ , gives the  $H_2$ -esters, b.p. 198—200°/13 mm., and 216—218°/12 mm., respectively, hydrolysed to dihydrohydnocarpic (I), b.p. 180—182°/1.3 mm., m.p. 63—5°, and dihydrochaulmoogric acid (II), b.p. 199—201°/1.3 mm., m.p. 73°, respectively. (I) is converted by Br and red P at room temp. and then at 100°, followed by aq.  $H_2SO_4$  or EtOH at 0°, into  $\alpha$ -bromodihydrohydnocarpic acid (III), a viscous liquid, or its Et ester (IV), b.p. 195°/3 mm., which rapidly blackens on exposure to light and air, respectively. (IV) and anhyd. NPhEt<sub>2</sub> at 215—220° for 72 hr. give Et  $\psi$ -hydnocarpate [ $\kappa$ -cyclopentyl- $\Delta^a$ -undecenoate], b.p. 168—170°/1 mm., hydrolysed to the acid, m.p. 57°, which is hydrogenated (PtO<sub>2</sub> in EtOH) to (I).  $\alpha$ -Bromodihydrochaulmoogric acid (V), m.p. 56—57° (Et ester, b.p. 204—205°/1 mm.), and  $\psi$ -chaulmoogric [ $\mu$ -cyclopentyl- $\Delta^a$ -tridecenoic] acid, m.p. 72° (Et ester, b.p. 190—195°/2.2 mm.), hydrogenated to (II), are similarly obtained.  $\alpha$ -Iododihydrochaulmoogric acid, m.p. 52°, from (V) and KI in boiling 96% of EtOH, gives a non-cryst. chloride and an amide, m.p. 109°. Aq. KOH and (III) at 100° afford  $\alpha$ -hydroxydihydrohydnocarpic acid, m.p. 75°, in 90% yield.  $\alpha$ -Hydroxydihydrochaulmoogric acid has m.p. 86°. (V) and KCN in boiling aq. EtOH afford  $\alpha$ -cyanodihydrochaulmoogric acid, m.p. 73°.  $\alpha$ -Anilino-, m.p. 128—129°, and  $\alpha$ -2-naphthylamino-, m.p. 142°, -dihydrohydnocarpic acid and  $\alpha$ -anilino-, m.p. 131—132°, and  $\alpha$ -2-naphthylamino-, m.p. 143—144°, -dihydrochaulmoogric acid are prepared by heating the Br-acids with  $NH_2Ar$ . (V) and NaSH in boiling aq. EtOH give  $\alpha$ -thioldihydrochaulmoogric acid, m.p. 66° after softening, oxidised by I to the disulphide, m.p. 70°. Distillation of dihydrohydnocarpamide with  $P_2O_5$  under 3 mm. gives dihydrohydnocarponitrile, b.p. 164—165°/0.5 mm. Dihydrochaulmoogronitrile, b.p. 192—195°/3 mm., is transformed by  $NH_2OH$  in boiling EtOH into dihydrochaulmoogramideoxime, m.p. 89°. (V) and  $MgMeI$  (3 mols.) in  $Et_2O$  give a complex mixture, b.p. 195—300°/1 mm., with acidic and ketonic properties. H. W.

**Mechanism of the Arndt-Eistert reaction.** C. Huggett, R. T. Arnold, and T. I. Taylor (*J. Amer. Chem. Soc.*, 1942, 64, 3043).—Eistert's mechanism (A., 1935, 332) for this reaction is confirmed by conversion of  $Ph^{13}CO_2H$  (giving, by decarboxylation by Cu chromite in quinoline,  $CO_2$  containing 2.51% of  $^{13}C$ ) into  $CH_2Ph^{13}CO_2H$  (giving by similar decarboxylation  $CO_2$  containing 2.53% of  $^{13}C$ ). R. S. C.

**Modification of Willgerodt's reaction.** E. Schwenk and (Miss) E. Bloch (*J. Amer. Chem. Soc.*, 1942, 64, 3051—3052).— $COArMe$  and S in boiling morpholine give  $CH_2Ar-CS-C_4H_8ON$ , hydrolysed (crude, if necessary) by alkali in boiling  $H_2O$  or EtOH to  $CH_2Ar-CO_2H$  (10—75% yield). Halogen or OMe may be present in Ar, but not  $NO_2$ ,  $NH_2$ , OH, or OAc. Phenyl-, m.p. 79—80°, *o*-, an oil, and *m*-anisyl-, m.p. 82—84°, *p*-bromo- and 2 : 5-dimethoxy-phenyl-, oils,  $\beta$ -naphthyl-, m.p. 108—109°, 2-phenanthryl-, an oil, and *o*-benzyl-oxyphenyl-, m.p. 118—119°, -thioacetmorpholide are thus prepared and hydrolysed. *o*-Benzyl-oxyacetophenone (prep. from *o*- $OH-C_6H_4-COMe$  and  $CH_2PhCl$  in boiling 15% NaOH), b.p. 182—184°/11 mm. (2 : 4-dinitrophenylhydrazones, m.p. 207—209; semicarbazones, m.p. 175—177°), and -phenylacetic acid, m.p. 97—99°, are described. R. S. C.

**Synthesis of derivatives of *s*-diphenylethane related to materials occurring naturally.** IV. Stilbene-2-acetic acid. S. Natelson and S. P. Gottfried (*J. Amer. Chem. Soc.*, 1942, 64, 2962—2963; cf. A., 1941, II, 133).—*o*- $CHPh:CH-C_6H_4-CHO$  (I) (improved prep.) and  $Al(OPr^i)_3-Pr^iOH$  give 2-hydroxy-, m.p. 92—93°, and thence ( $SOCl_2$ ) 2-chloro-methylstilbene, b.p. 170—185°/15 mm., and ( $NaCN$ -aq. EtOH) stilbene-2-acetonitrile, m.p. 81—82°, which in boiling conc. HCl-AcOH gives stilbene-2-acetic acid (II), m.p. 105—106°, and its amide, m.p. 152—153° [in conc. HCl-AcOH yields (II)]. The oxazolone from (I) and hippuric acid with aq.  $Ba(OH)_2$  at 85° gives  $\alpha$ -benzamido-*o*-styrylcinnamic acid, m.p. 199—202°, whence (II) is obtained in poor yield by NaOH and then  $H_2O_2$ . 4 : 5 : 1 : 2-(OMe)<sub>2</sub> $C_6H_3(CO)_2O$ , 3 : 4 : 1-(OMe)<sub>2</sub> $C_6H_3-CH_2-CO_2H$ , and NaOAc at 230° give 4 : 5 : 3' : 4'-tetramethoxy- $\alpha$ -benzylidenephthalide, m.p. 179—180°, reduced by Na-Hg in aq. NaOH to 4 : 5 : 3' : 4'-tetramethoxybenzylphthalide, m.p. 146—148°, which, when dissolved in KOH-EtOH, evaporated, and heated at 180° yields 4 : 5 : 3' : 4'-tetramethoxystilbene-2-carboxylic acid, m.p. 209—211°. (II) does not yield a lactone. R. S. C.

**Synthetic anthelmintics.** IV. Synthesis of lactones similar to desmotroposantonin. K. Paranjpe, N. L. Phalnikar, and K. S. Nargund. V.  $\gamma$ -*p*-Alkoxyphenylbutyrolactones. J. J. Trivedi and K. S. Nargund (*J. Univ. Bombay*, 1942, 11, A, Part 3, 124—126, 127—130).—IV. 1-Keto-7-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene, Zn, and  $CH_2Br-CO_2Et$  in PhMe yield Et 1-hydroxy-7-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylacetate, m.p. 50° (free acid, m.p. 127°), which is dehydrated ( $P_2O_5$  in  $C_6H_6$ ) and then hydrolysed

(cold alkali) to 7-methoxy-3 : 4-dihydro-1-naphthylacetic acid, m.p. 141—5°, converted by 60%  $H_2SO_4$  at room temp. into the lactone, m.p. 60°, of 2-hydroxy-7-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylacetic acid, demethylated (HBr-AcOH) to the OH-lactone, b.p. 240°/10 mm. 1-Keto-5-methoxy-8-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 195°/50 mm. (from 2 : 5 : 1-OMe- $C_6H_3Me-[CH_2]_3-CO_2H$  and  $P_2O_5$  in  $C_6H_6$ ), similarly yields 1-hydroxy-5-methoxy-8-methyl-1 : 2 : 3 : 4-tetrahydro-1-naphthylacetic acid, m.p. 90°, 5-methoxy-8-methyl-3 : 4-dihydro-1-naphthylacetic acid, b.p. 192°/50 mm., and 2-hydroxy-5-methoxy-, b.p. 190°/20 mm., and 2 : 5-dihydroxy-8-methyl-1 : 2 : 3 : 4-tetrahydro-1-naphthylacetic acid lactone, b.p. 180°/40 mm.

V.  $(CH_2CO)_2O$ , PhOAlk, and  $AlCl_3$  in  $PhNO_2$  give 80—90% of  $\gamma$ -keto- $\gamma$ -*p*-ethoxy-, -*n*-propoxy-, -*n*-butoxy-, -isobutoxy-, -isoamyloxy-, and -*n*-hexyloxy-phenylbutyric acid, m.p. (to clear liquids) 137—138°, 118—119°, 112, 131—132°, 120°, and 109°, respectively, turbid liquids being formed 4—5° below these [semicarbazones, m.p. 189°, 178—179°, 171—172°, 188—189°, 185°, and 181°, respectively; Me esters, m.p. 50—51, 58°, 43—44°, —, —, and —, respectively; Et esters, m.p. 52°, —, (b.p.) 240°/20 mm., —, —, and —, respectively], reduced (Na + EtOH) to the  $\gamma$ -OH-acids, m.p. —, 101°, 80, 73°, 83—84°, and —, respectively, which yield the  $\gamma$ -*p*-alkoxyphenylbutyrolactones, m.p. 73—74°, 64°, 63—64°, (b.p.) 198°/5 mm., 74°, and 66—67°, respectively. The CO-acids are also obtained from  $p$ - $OH-C_6H_4-CO-[CH_2]_2-CO_2Et$ , AlkBr, and  $K_2CO_3$  in  $COMe_2$ . A. Li.

**Mechanism of the reaction between hindered carbonyl compounds and the Grignard reagent.** II. R. T. Arnold and R. W. Liggett (*J. Amer. Chem. Soc.*, 1942, 64, 2875—2877; cf. A., 1942, II, 142).—Cleavage of allyl ethers by, or addition of, Grignard reagents depends on the amount of steric hindrance around the CO. 1-Bromo-2 : 3-dimethylnaphthalene (prep. from 2 : 3- $C_{10}H_6Me_2$  by  $Br-CHCl_3-CCl_4$  at 0°—room temp.), m.p. 63—64°, with  $Mg-MgEtBr$  (trace) in  $Et_2O$  and then  $CO_2$  gives 2 : 3-dimethyl-1-naphthoic acid (I), m.p. 167—168°, the allyl ester (prep., as the allyl esters below, from the Na salt by  $CH_2=CH-CH_2Br$  in xylene), m.p. 33—34°, b.p. 155—160°/2 mm., of which with  $MgPhBr$  gives 97% of (I) and 82.4% of  $CH_2=CH-CH_2Ph$  (II). Allyl triphenylacetate, m.p. 85—85.5°, and  $MgPhBr$  give 93% of  $CPh_3-CO_2H$ .  $CHMeEt-CO_2Et$  with  $NaCPh_3$  and then  $CH_2PhBr$  gives Et  $\alpha$ -benzyl- $\alpha$ -methyl-*n*-butyrate, b.p. 127—130°/9—10 mm., which affords, by way of the acid (III), the allyl ester, b.p. 139—140°/8 mm., converted by  $MgPhBr$  into (III) (87%) and (II) (70%). Allyl *aa*-diphenylpropionate, b.p. 175—177°/8 mm., with  $MgPhBr$  gives  $CPh_2Me-CO_2H$  (88%). Allyl  $\beta$ -ethyl-*n*-hexoate (prep. from the alcohol and acid chloride in  $C_6H_5N-CHCl_3$ ), b.p. 79—79.5°/8 mm., and  $MgPhBr$  give the acid (30%), (II) (26%), and impure carbinol (~49%). Allyl  $\alpha$ -ethyl-*n*-butyrate (25.3 g.), b.p. 165—167°, with  $MgPhBr$  gives  $CH_2Et-CO_2H$  (4.5), (II) (9.0), and a carbinol (10.3 g.), b.p. 170—175°/8 mm., converted by  $HCO_2H$  into  $\gamma$ -benzhydrylidene-*n*-pentane. Allyl hexahydrobenzoate (prep. from the acid chloride), b.p. 103—104°/18 mm., and  $MgPhBr$  (2 mols.) give only the carbinol, dehydrated by  $HCO_2H$  to benzhydrylidene-cyclohexane, m.p. 82—83°. Et cyclohexanone-2-carboxylate with  $NaOEt-EtOH$ -xylene- $PhSO_3Et$  gives Et 2-ethyl-cyclohexanone-2-carboxylate, b.p. 125—130°/18 mm. (semicarbazone, m.p. 156.5—157°), which by successive treatment with  $H_2$ -Raney Ni at 175—200°/2000 lb.,  $P_2O_5-C_6H_6$ ,  $H_2$ -Raney Ni at 150°/1800 lb. (gives an ester, b.p. 100—110°/10—15 mm.), KOH-MeOH,  $SOCl_2$ , and esterification gives allyl 1-ethylcyclohexanecarboxylate, b.p. 97—98°/8 mm. With  $MgPhBr$  this gives only the carbinol. R. S. C.

**Preparation of *o*-hydrazinobenzoic acids and indazolones by reduction of diazotised anthranilic acids by sulphurous acid.** K. Pfannstiel and J. Janecke (*Ber.*, 1942, 75, [B], 1096—1107).—*o*- $CO_2H-C_6H_4-NH-NH_2.HCl$ , new m.p. 189—190°, is obtained in 84% yield from *o*- $CO_2H-C_6H_4-N_2Cl$  and aq.  $SO_2$  through which passage of  $SO_2$  is continued; the acid has m.p. 247° (m.p. of the indazolone). The following 2-hydrazinobenzoic acids are obtained analogously: 4-nitro-, m.p. 237° [hydrochloride, m.p. 208—209° (decomp.)];  $CHPh$  derivative, m.p. 251° (decomp.); 5-nitro-, m.p. 264—275° (decomp.), darkens greatly at 216° [hydrochloride, m.p. as for acid;  $CHPh$  derivative, m.p. 253° (decomp.)], also obtained from 5 : 2 : 1- $NO_2-C_6H_3Cl-CO_2H$  and  $N_2H_4.H_2O$  in boiling abs. EtOH; 6-chloro-, which could not be recryst. [hydrochloride, m.p. 227° (decomp.) (sinters 205°)] on account of ready ring closure, transformed by boiling  $PhCHO$  into 5-chloro-4-hydroxy-3-phenylcinnoline, m.p. >300°. The indazolones [except (I) and (II) (below)] are obtained from the *o*-hydrazinobenzoic acids and their hydrochlorides by boiling, very dil. HCl. Thus are obtained indazolone, m.p. 247° ( $Ac_2$  derivative, m.p. 135°), 4-nitro- (I), also hydrated, m.p. 245° (decomp.), alters >200° [hydrochloride, m.p. 245° (decomp.)], 5-nitro-, m.p. 275° (decomp.), darkens at 270, 6-nitro-, unstable orange-red needles or stable yellow prisms (+1MeOH), orange-red needles or lemon-yellow, compact crystals (+1AcOH), orange-red hydrated needles, m.p. 244° (for all forms), and 7-nitro- (II), m.p. 295—305° (hydrochloride), and 4-chloro-indazolone (anhyd. and +0.5 $H_2O$ ), m.p. 263° [hydrochloride, m.p. 231° (decomp.)], hydrolysed by  $H_2O$ . Reduction of the appropriate  $NO_2$ -compound by  $SnCl_2$  and HCl gives 4-amino-, m.p. 245° (decomp.), 5-amino- (+  $H_2O$ ), m.p. 290° (decomp.),

6-amino-, m.p. 287° (decomp.), and 7-amino-, m.p. 260° (decomp.), becomes discoloured at 230°, -indazolone dihydrochlorides. H. W.

**Local anæsthetics. II. Alkoxybenzoates of  $\beta$ -monoalkylamino- $\beta$ -methylpropan- $\alpha$ -ols and  $\beta$ -monoalkylaminobutan- $\alpha$ -ols.** J. S. Pierce, J. M. Salsbury, W. W. Haden, and L. H. Willis (*J. Amer. Chem. Soc.*, 1942, **64**, 2884—2885; cf. A., 1942, II, 404).— $\text{NH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$  or  $\text{NH}_2\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{OH}$  with  $\text{AlkBr}$  at 100° gives  $\beta$ -ethyl-, m.p. 72—73°, b.p. 167—170°,  $\beta$ -*n*-propyl-, m.p. 56—57.5°, b.p. 185—188°,  $\beta$ -*n*-amyl-, m.p. 56—59°, b.p. 218—221°,  $\beta$ -*n*-hexyl-, m.p. 62—62.5°, b.p. 235—238°,  $\beta$ -*n*-heptyl-, m.p. 50—52°, b.p. 253—256°,  $\beta$ -*n*-octyl-, m.p. 68—69°, b.p. 202—204°, and  $\beta$ -iso-butyl-, m.p. 48—49°, b.p. 184—187°,  $\beta$ -isoamyl-, m.p. 73—74°, b.p. 214—217°,  $\beta$ -allyl-, b.p. 183—187°, and  $\beta$ -benzyl-, m.p. 53—57°, b.p. 277—280°, -aminoisobutyl alcohol (cf. Kremer *et al.*, A., 1942, II, 283),  $\beta$ -ethyl-, b.p. 177—179°,  $\beta$ -*n*-propyl-, b.p. 192—193°,  $\beta$ -*n*-, b.p. 210—213°, and  $\beta$ -iso-butyl-, b.p. 195—198°,  $\beta$ -*n*-, b.p. 227—230°, and  $\beta$ -iso-amyl-, b.p. 221—224°,  $\beta$ -*n*-hexyl-, b.p. 247—252°,  $\beta$ -*n*-heptyl-, b.p. 263—266°,  $\beta$ -allyl-, b.p. 194—197°, and  $\beta$ -benzyl-, b.p. 283—285°, -amino-*n*-butyl alcohol. The derived hydrochlorides with  $\text{RCOCl}$  at, successively, 100°, 130°, and 150° give  $\beta$ -*n*-butylaminoisobutyl *p*-anisoate hydrochloride, m.p. 154—155°,  $\beta$ -*n*-amyl-, m.p. 128—129°, and  $\beta$ -*n*-hexyl-aminoisobutyl *p*-ethoxybenzoate hydrochloride, m.p. 135—136°,  $\beta$ -*n*-butylaminoisobutyl *o*-, m.p. 118—120°, and *m*-ethoxy-, m.p. 106—108°, *p*-*n*-propoxy-, m.p. 98—100°, *p*-, m.p. 125—127°, and *o*-*n*-butoxy-, m.p. 91—94°, *p*-*n*-amyloxy-, m.p. 125—126°, *p*-*n*-hexyloxy-, m.p. 125.5—127°, and *p*-*n*-heptyloxy-benzoate hydrochloride, m.p. 117—118°,  $\beta$ -*n*-amylaminoisobutyl *m*-ethoxy-, m.p. 73—76°, *p*-*n*-propoxy-, m.p. 103—106°, *p*-*n*-amyloxy-, m.p. 103—104°, and *p*-*n*-heptyloxy-benzoate hydrochloride, m.p. 105—106°,  $\beta$ -*n*-hexylaminoisobutyl *p*-*n*-propoxy-, m.p. 118—120°, *p*-*n*-butoxy-, m.p. 122—123°, and *p*-*n*-heptyloxy-benzoate hydrochloride, m.p. 105—107°,  $\beta$ -*n*-propylaminoisobutyl *p*-*n*-butoxy-, m.p. 105—107°, *p*-*n*-amyloxy-, m.p. 112—113°, and *p*-*n*-heptyloxy-benzoate hydrochloride, m.p. 108—110°,  $\beta$ -ethyl-, m.p. 136—138°, and  $\beta$ -benzyl-aminoisobutyl *p*-*n*-butoxy-benzoate hydrochloride, m.p. 161—162°,  $\beta$ -benzylaminoisobutyl *p*-*n*-amyloxybenzoate hydrochloride, m.p. 139—140°,  $\beta$ -ethyl-, m.p. 184—185°,  $\beta$ -*n*-butyl-, m.p. 134—135°,  $\beta$ -*n*-hexyl-, m.p. 135—136°, and  $\beta$ -benzyl-amino-*n*-butyl *p*-ethoxybenzoate hydrochloride, m.p. 181—184°,  $\beta$ -*n*-butylamino-*n*-butyl *p*-*n*-, m.p. 129—131°, and *p*-iso-propoxy-, m.p. 119—121°, and *p*-*n*-butoxy-benzoate hydrochloride, m.p. 114—116°,  $\beta$ -*n*-hexylaminobutyl *p*-*n*-propoxybenzoate hydrochloride, m.p. 112—114°, and  $\beta$ -*n*-propylamino-*n*-butyl *p*-*n*-heptyloxybenzoate hydrochloride, m.p. 108—109°. B.p. (not m.p.) are corr.

R. S. C.

**3-Bromosalicylic acid.**—See A., 1943, II, 146.

**Veratrole and methylenedioxybenzene series.** R. T. Arnold and F. Bordwell (*J. Amer. Chem. Soc.*, 1942, **64**, 2983—2986).—*pK* (in 50% EtOH) recorded below show that the structure of the  $\text{C}_6\text{H}_8$  rings in the veratrole and  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_4$  series is very similar. Me veratrate, m.p. 58—59°, b.p. 165°/15 mm., and  $\text{HNO}_3$  (*d* 1.59) in AcOH at 0° give 6:3:4:1- $\text{NO}_2\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CO}_2\text{Me}$ , m.p. 144—145°, hydrogenated (Raney Ni; MeOH; 110°/1000 lb.) to the  $\text{NH}_2$ -ester, m.p. 128—129° (lit. 133°), which yields (diazo-reaction;  $\text{CuSO}_4\cdot\text{H}_2\text{SO}_4$ ) the 6-OH-ester, m.p. 95—96°, and thence the 6-OH-acid, m.p. 204—205° (decomp.) (lit. 201—202°) (*pK* 4.60). 6:3:4:1- $\text{NH}_2\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CHO}$  yields 6:3:4:1-OH- $\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CHO}$ , m.p. 106—107° (*pK* 9.12), the oxime, m.p. 146—147°, of which in boiling  $\text{Ac}_2\text{O}$  gives 6-hydroxyveratronitrile, sinters 120°, m.p. 142—145° (decomp.) (*pK* 8.69). 5-Nitro-4-hydroxyveratrole, m.p. 142—143° (*pK* 8.33), is obtained from 5:1:2:4- $\text{NO}_2\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{NHAc}$  by hydrolysis and subsequent diazo-reaction. 36% of 3:4:6:1- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2(\text{OH})\cdot\text{CO}_2\text{Me}$ , m.p. 100—101°, is obtained from the  $\text{NH}_2$ -ester by a diazo-reaction as above. Similar reactions give 6-hydroxypiperonal (I), m.p. 125—126° (*pK* 8.90), and thence the oxime, m.p. 142.5—143.5°, and 6-hydroxypiperonitrile, m.p. 220—225° (decomp.) (*pK* 8.41).  $\text{Ac}_2\text{O}$  and (I) in  $\text{C}_5\text{H}_5\text{N}$  at 35—40° give 6-acetoxypiperonal, m.p. 126—127°, oxidised by  $\text{KMnO}_4$ - $\text{COMe}_2\cdot\text{H}_2\text{O}$  to 6-acetoxypiperonylic acid, m.p. 149—150°, which is obtained only with difficulty from the OH-acid (*pK* 4.58). 2-Nitro-4:5-methylenedioxyphenol, m.p. 82.5—84°, is obtained from the  $\text{NO}_2$ -amine by a diazo-reaction. 3:4:1- $\text{CMe}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{NO}_2$  with  $\text{H}_2$ -Raney Ni in EtOH and then  $\text{Ac}_2\text{O}$ - $\text{NaOAc}$  gives 3:4-isopropylidenedioxyacetanilide, m.p. 108.5—109.5°. 4:5:2:1- $\text{CMe}_2\text{O}_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)\cdot\text{NH}_2$ , m.p. 127—128°, gives (diazo-reaction) a little 2-nitro-4:5-isopropylidenedioxyphenol, m.p. 148—149° (*pK* 8.68 in 67% EtOH). Veratric and piperonylic acid have *pK* 6.21 and 6.19, respectively.

R. S. C.

**Identification of *o*- and *p*-sulphobenzoic acids as their *S*-benzylthiuronium salts.** E. Campaigne and C. M. Suter (*J. Amer. Chem. Soc.*, 1942, **64**, 3040—3041).— $\text{p-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , prepared by way of the Ba salt from  $\text{p-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  by alkaline  $\text{KMnO}_4$ , with *S*-benzylthiuronium chloride gives *S*-benzylthiuronium *H* *p*-sulphobenzoate, m.p. 212.6—214.4° (corr.).  $\text{o-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  gives the di-*S*-benzylthiuronium salt, m.p. 205.5—206.5° (corr.). The *m*-acid gives a sol. salt.

R. S. C.

**Preparation of ethyl ethylmalonate and  $\Delta^1$ -cyclohexenylmalonate from the corresponding oxaloacetates.** P. Galimberti [in part with

S. Ponzini] (*Gazzetta*, 1942, **72**, 125—130).— $\text{Et}_2\text{C}_2\text{O}_4$  (I),  $\text{Pr}^a\text{CO}_2\text{Et}$ , and  $\text{EtOH}\cdot\text{NaOEt}$  (II) at 60°, followed by  $\text{H}_2\text{SO}_4$ , give  $\text{Et}_2\alpha$ -oxalobutyrate, an oil, which at 160° loses CO, giving  $\text{CHEt}(\text{CO}_2\text{Et})_2$ , cyclohexanone,  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ , and Zn in boiling  $\text{C}_6\text{H}_6$  give Et 1-hydroxycyclohexylacetate, which with  $\text{KHSO}_4$  gives Et  $\Delta^1$ -cyclohexenylacetate. This with (I) and (II), followed by  $\text{H}_2\text{SO}_4$ , gives  $\text{Et}_2\Delta^1$ -cyclohexenylmalonate, an oil, which at 135—140° loses CO, giving  $\text{Et}_2$  cyclohexenylmalonate.  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$ , (I), and (II), followed by EtI, give  $\text{Et}_2\alpha$ -oxalo- $\alpha$ -phenylbutyrate, b.p. 280—285°.

E. W. W.

**Carboxylation. IV. Direct introduction of the chloroformyl ( $\cdot\text{COCl}$ ) group into alicyclic and aliphatic acid chlorides.** M. S. Kharasch, K. Eberly, and M. Kleiman (*J. Amer. Chem. Soc.*, 1942, **64**, 2975—2977; cf. A., 1942, II, 393).—cycloHexane and  $\text{ClCO}_2\text{CCl}_3$  at 225° give 3% of cyclohexane-1:1-dicarboxyl dichloride (I), identified by hydrolysis to the acid and conversion into the diamide, m.p. 261° (lit. 237°); absence of hexahydrobenzoyl chloride is due to the fact that this chloride gives similarly 81% of (I). Similarly  $\text{Pr}^b\text{COCl}$  gives 70% of  $\text{CMe}_2(\text{COCl})_2$ ,  $\text{CHEt}_2\cdot\text{COCl}$  gives 90% of  $\text{CEt}_2(\text{COCl})_2$ ,  $\text{CHEtBu}^a\cdot\text{COCl}$  gives 30% of  $\text{CEtBu}(\text{COCl})_2$ ,  $\text{EtCOCl}$  gives 15% of  $\text{CHMe}(\text{COCl})_2$ , and  $\text{CH}_2\text{Ph}\cdot\text{COCl}$  gives 2% of  $\text{CHPh}(\text{COCl})_2$ , but  $\text{AcCl}$  gives no  $\text{CH}_2(\text{COCl})_2$ . The ease of  $\alpha$ -substitution is thus  $\text{CHR}_2\cdot\text{COCl} > \text{CH}_2\text{R}\cdot\text{COCl} > \text{AcCl}$ .

R. S. C.

**Characteristic reaction of phenylmethylhydrazones of aromatic aldehydes.** R. Ciusa and M. Di Fonzo (*Gazzetta*, 1942, **72**, 166—169).—The reaction (cf. Ciusa *et al.*, A., 1922, i, 474) whereby  $\text{CHPh}\cdot\text{N}\cdot\text{NPhMe}$  with  $\text{HCl}\cdot\text{Et}_2\text{O}$  gives  $\text{CHPh}\cdot\text{N}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NH}_2$  (which with  $\text{PhCHO}$  gives its  $\text{CHPh}\cdot$  derivative) is carried out with substituted compounds. *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NPhMe}$  gives a similar dimeride, m.p. 233° (*p*-nitrobenzylidene derivative, m.p. 195°), and 3:4:1- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{N}\cdot\text{NPhMe}$  yields a dimeride, m.p. 178°, which with *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  gives, by condensation and replacement, bis-*p*-nitrobenzaldehyde *p*'*p*'-piperonylidenebisphenylmethylhydrazone, m.p. 200°.

E. W. W.

**Catalytic reduction of *N*-phenylnitrophenylnitrones.** A. Gandini (*Gazzetta*, 1942, **72**, 28—37).—With Pt-black in  $\text{Et}_2\text{O}$ , *o*- and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NPh}\cdot\text{O}$  with 4  $\text{H}_2$  give orange-coloured resinous products, but with 1—3  $\text{H}_2$  they also give small quantities of *N*-phenyl-*o*-(I), m.p. 133°, and *p*-amino-, m.p. 136—138°, and *o*-, m.p. 132° [mixed m.p. with (I), 110—118°], and *p*-hydroxylamino-nitron, m.p. 116—117°. *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NPh}\cdot\text{O}$  with 1 or 2  $\text{H}_2$  gives uncrystallisable products, but with 3 or, better, 4  $\text{H}_2$  gives *N*-phenyl-*N*-*m*-aminobenzylhydroxylamine, m.p. 122.5—123°.

E. W. W.

**Bromination of ketones.**—See B., 1943, II, 108.

**Synthesis of ketones having a diethylstilbestrol carbon skeleton.**—See B., 1943, III, 88.

**Acetylphenylcarbinol and benzoylmethylcarbinol. Simultaneous formation starting from  $\beta$ -chloro- $\alpha$ -phenylpropan- $\alpha$ -one or from  $\alpha$ -chloro- $\alpha$ -phenylpropan- $\beta$ -one. Their identification.** G. Richard (*Compt. rend.*, 1942, **214**, 673—675; cf. Favorski *et al.*, A., 1935, 622).—With *N*-NaOH in 50% aq. EtOH,  $\text{CHPhCl}\cdot\text{COMe}$  (I) (rapidly at room temp.) or  $\text{CHMeCl}\cdot\text{COPh}$  (slowly at 60°) gives  $\text{COPh}\cdot\text{COMe}$ , b.p. 101—102°/12 mm. (semicarbazone, m.p. 229°), and a mixture of  $\text{OH}\cdot\text{CHPh}\cdot\text{COMe}$  (separated as  $\text{NaHSO}_3$  compound), b.p. 122—123°/12 mm. [semicarbazone, m.p. 181—182°; benzoate, new m.p. 108—109°; converted by  $\text{SOCl}_2$  in  $\text{CCl}_4$  into (I), which with  $\text{C}_6\text{H}_6$  ( $\text{AlCl}_3$ ) yields  $\text{CHPh}_2\cdot\text{COMe}$ ], and  $\text{OH}\cdot\text{CHMe}\cdot\text{COPh}$ , b.p. 128—132°/12 mm. (semicarbazone, m.p. 193°).

A. Li.

**Condensation of methylsuccinic anhydride with tolyl methyl ethers.** B. L. Bhatt and K. S. Nargund (*J. Univ. Bombay*, 1942, **11**, A, Part 3, 131—133).—With methylsuccinic anhydride and  $\text{AlCl}_3$  in  $\text{PhNO}_2$  ( $\text{CS}_2$  or  $\text{C}_2\text{H}_2\text{Cl}_4$  gives the same products in lower yields), *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$  yields  $\gamma$ -keto- $\gamma$ -6-methoxy-*m*-tolyl- $\alpha$ -methylbutyric acid, m.p. 124° [*Ag* salt; semicarbazone, m.p. 170° (decomp.)]; *Me*, b.p. 190—192°/13 mm., and *Et* ester, b.p. 197—198°/10 mm., oxidised ( $\text{NaOBr}$ ) to 4:3:1- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{H}$ , *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$  yields  $\gamma$ -keto- $\gamma$ -5-methoxy-*o*-tolyl- $\alpha$ -methylbutyric acid, m.p. 113° (semicarbazone, m.p. 172—173°; *Me*, b.p. 187—189°/12 mm., and *Et* ester, b.p. 193°/11 mm.), oxidised to 4:2:1- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{H}$ , and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$  yields  $\gamma$ -keto- $\gamma$ -4-methoxy-*m*-tolyl- $\alpha$ -methylbutyric acid, m.p. 129° (no semicarbazone; *Me*, b.p. 176—180°/9 mm., and *Et* ester, b.p. 160°/3 mm.), oxidised to 2:5:1- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{H}$ . The CO-acids give pyrylium derivatives with *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  and  $\text{HCl}$ .

A. Li.

**Factors determining the course and mechanism of Grignard reactions. V. Effect of metallic halides on the reaction of Grignard reagents with phenyl styryl ketone and benzophenone.** M. S. Kharasch and D. C. Sayles (*J. Amer. Chem. Soc.*, 1942, **64**, 2972—2975; cf. A., 1942, II, 48).—Metallic chlorides (2—5%) do not affect the ratio of 1:2 to 1:4 addition of  $\text{MgMeBr}$  (1.4 mols.) to  $\text{CHPh}\cdot\text{CH}\cdot\text{COPh}$  (I), but change the nature of the products. In absence of a chloride at 0—5°,  $\text{CHPhMe}\cdot\text{CH}_2\cdot\text{COPh}$  (II) (59%) and  $\delta$ -benzoyl- $\alpha$ - $\gamma$ -triphenyl- $\Delta^{\alpha\gamma}$ -*n*-hexadiene (III) (41%), m.p. 176°, are formed; 1 mol.-% of  $\text{FeCl}_3$  leads to (II) (66%), (III) (9%), ( $\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COPh}$ )<sub>2</sub>, forms (IV) (21%), m.p. 197°, and (V) (4%),

m.p. 276°; CuCl leads to (II) (69%), (III) (24%), and (IV) (7%); MnCl<sub>2</sub> leads to (II) (73%) and (III) (27%); CoCl<sub>2</sub> yields only (IV) (82%) and (V) (18%). (III) is formed by addition of (I) to (II) under the influence of MgMeBr, and also of C<sub>5</sub>H<sub>5</sub>N, NMe<sub>3</sub>, or NaOEt; its formation is entirely suppressed only if 3 mols. of MgMeBr are used. At 20–25°, MgEtBr and CPh<sub>2</sub> with or without CoCl<sub>2</sub> give only CPh<sub>2</sub>Et·OH, but at –12° 50% of (CPh<sub>2</sub>·OH)<sub>2</sub> is obtained in presence of 2 mol.-% of CoCl<sub>2</sub>, showing that the stability of CoEtCl is the determining factor. Metallic halides have little effect on the 1:4 addition of MgPhBr to (I), but 2–5 mol.-% of FeCl<sub>3</sub> or CoCl<sub>2</sub> gives 2–5% of (V). MgEtBr and (I) at 25° give 60% of CPh·CH<sub>2</sub>·CHPhEt (removed by acethydrazidepyridinium chloride) and 40% of *α*-diphenyl-Δ<sup>4</sup>-n-penten-γ-ol (VI), an oil (cf. Kohler, A., 1907, i, 1050); at –25° somewhat less (VI) is formed. (VI) is determined by titration by KMnO<sub>4</sub>. In one experiment using MnCl<sub>2</sub> a substance, C<sub>32</sub>H<sub>32</sub>O<sub>2</sub>, m.p. 136° (2:4-dinitrophenylhydrazones), was isolated.

R. S. C.

**α-Alkylaminoacylophenones.**—See B., 1943, II, 108.

**Action of phosphoric oxide on phenyl esters. Mechanism of the Fries reaction.** A. Schönberg and (Miss) A. Mustafa (J.C.S., 1943, 79–80).—PhOBz and P<sub>2</sub>O<sub>5</sub> in PhNO<sub>2</sub> at 150° give *p*-C<sub>6</sub>H<sub>4</sub>Bz·OBz and PhOH (converted into Ph phosphates). *m*-Tolyl and *α*-C<sub>10</sub>H<sub>7</sub> benzoate similarly give 6-benzoyl-*m*-tolyl and 4-benzoyl-1-naphthyl benzoate, respectively. Results support the view of Rosenmund *et al.* (A., 1928, 1010) on the mechanism of the Fries reaction.

A. T. P.

**Ene-diols. XI. Vinylogues of ethylene and acetylene glycols.** R. C. Fuson, D. J. Byers, and A. I. Rachlin (J. Amer. Chem. Soc., 1942, 64, 2891–2893; cf. A., 1943, II, 35).—CH<sub>2</sub>:CMes·COMes (I) (Mes = mesityl) and Mg + MgI<sub>2</sub> in hot C<sub>6</sub>H<sub>6</sub> give *αβεζ*-tetramesityl-Δ<sup>4,6</sup>-n-hexadiene-*αζ*-diol (II) (94%), m.p. 207–208° (diacetate, m.p. 217.5–218.5°), the structure of which is proved by atm. oxidation in COMe<sub>2</sub> to (CH<sub>2</sub>:COMes)<sub>2</sub> and MesOH. Boiling HCl–EtOH ketonises (II) to *αβεζ*-tetramesityl-n-hexane-*αζ*-dione, m.p. 259–261°, which with MgEtBr in Et<sub>2</sub>O–C<sub>6</sub>H<sub>6</sub> regenerates (II). With KMnO<sub>4</sub> in COMe<sub>2</sub>, (II) yields (I) and a little yellow *αβεζ*-tetramesityl-Δ<sup>4,6</sup>-n-hexadiene-*αζ*-dione (III), m.p. 282–284°; with Pb(OAc)<sub>4</sub> in C<sub>6</sub>H<sub>6</sub>, (III) is the main and (I) the subsidiary product. H<sub>2</sub>–PtO<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> or Zn dust in AcOH at 100° reduces (III) to colourless *αβεζ*-tetramesityl-Δ<sup>4,6</sup>-n-hexatriene-*αζ*-diol (IV), m.p. 252–253°, unstable [with boiling Ac<sub>2</sub>O gives a diacetate, m.p. 273–274°, obtained directly from (III) by H<sub>2</sub>–PtO<sub>2</sub> and a little ZnCl<sub>2</sub>–HCl in Ac<sub>2</sub>O], which with aq. H<sub>2</sub>O<sub>2</sub> regenerates (III). (IV) and *αβεζ*-tetramesityl-Δ<sup>4,6</sup>-n-hexene-*αζ*-dione, m.p. 201°, are interconvertible by HCl–EtOH and MgEtBr.

R. S. C.

**Velocity of formation of oximes of cyclohexanone and its derivatives.**—See A., 1943, I, 132.

**New benzyl derivative of 4-methylcyclohexanone.** A. R. Poggi (Gazzetta, 1942, 72, 16–18).—4-Methylcyclohexanone, CH<sub>2</sub>PhCl, and NaNH<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> give the 2-CH<sub>2</sub>Ph derivative, b.p. 169.5–170°/17 mm. [oxime, m.p. 129° (softens 125°); semicarbazone A, m.p. 196° (softens 160°), B, m.p. 174° (softens 169°); 2:4-dinitrophenylhydrazones, m.p. 146° (softens 141°)].

E. W. W.

**Preparation of β-6-keto-2-methyl-Δ<sup>1</sup>-cyclohexenylpropionic acid.** E. Schwenk and (Miss) E. Bloch (J. Amer. Chem. Soc., 1942, 64, 3050–3051).—Adding (CH<sub>2</sub>O)<sub>3</sub> to CH<sub>2</sub>Ac·CO<sub>2</sub>Me and piperidine at 60–80°, adding Na<sub>2</sub>SO<sub>4</sub> and keeping in the cold, and hydrolysing the product by boiling NaOEt–EtOH gives *Me* 3-methyl-Δ<sup>2</sup>-cyclohexenone-4-carboxylate (I) (37%), b.p. 135°/2 mm. (semicarbazone, m.p. 168–170°), and some 3-methyl-Δ<sup>2</sup>-cyclohexenone, b.p. 70°/2 mm. With NaOMe and Br·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>Me in boiling MeOH, (I) gives *Me* β-6-keto-3-carbomethoxy-2-methyl-Δ<sup>1</sup>-cyclohexenylpropionate (83%), b.p. 170–180°/1 mm. (semicarbazone, m.p. 145–148°). This and the corresponding Et ester, b.p. 184–186°/2 mm. [similarly prepared (70%); 2:4-dinitrophenylhydrazones, m.p. 120–122°], are converted by boiling 42% HI into β-6-keto-2-methyl-Δ<sup>1</sup>-cyclohexenylpropionic acid, m.p. 79–81°, which could not be cyclised to a hydrindone derivative.

R. S. C.

**Macrocyclic ring systems. II. Synthesis of *ν*-muscone.** H. Hunsdiecker (Ber., 1942, 75, [B], 1197–1201).—CHMe·CH·CO<sub>2</sub>Et and CH<sub>2</sub>(COMe)<sub>2</sub> are condensed (NaOEt in EtOH) to the tricarbonylic ester, which is hydrolysed, decarboxylated, and partly esterified to a mixture (I) of *Me* H β-methylglutarate and β-methylglutaric anhydride. Mixed electrolysis (Pt cathode, Ni anode, MeOH–NaOMe) of (I) and *κ*-methoxyundecic acid, f.p. 32.7°, b.p. 170°/4 mm. (from Br·[CH<sub>2</sub>]<sub>10</sub>·CO<sub>2</sub>H), gives *Me*<sub>2</sub> βε-dimethylhexane-*αζ*-dicarboxylate, b.p. 115°/1.5 mm., *Me* *ν*-methoxy-β-methyltetradecoate (II), b.p. 146°/1.5 mm. (yield 34.4%), and *αν*-dimethoxyeicosane, b.p. 185–193°/1.5 mm. (II) and 40% HBr–AcOH at 150° give *ν*-bromo-β-methyltetradecoic acid, b.p. 207°/3 mm., m.p. 51–52°, transformed (SOCl<sub>2</sub>) into the chloride, which is condensed with CHAcNa·CO<sub>2</sub>Et giving a product converted by NaOMe at room temp. into *Me* *α*-bromo-β-keto-δ-methylhexadecoate (III), m.p. 22°. (III) is converted into the I-derivative, which is added gradually to a boiling suspension of anhyd. K<sub>2</sub>CO<sub>3</sub> in boiling COMeEt, giving *Me* 2-keto-4-methylcyclopentadecanecarboxylate, b.p. 162°/1 mm.,

hydrolysed and decarboxylated by 80% H<sub>2</sub>SO<sub>4</sub> at room temp. to *ν*-muscone, b.p. 132–134°/0.8 mm. (semicarbazone, m.p. 133–133.5°).

H. W.

**Fluorenones and diphenic acids. IX. Establishment of authentic 1- and 4-bromofluorenones.** E. H. Huntress, K. Pfister, tert., and K. H. T. Pfister (J. Amer. Chem. Soc., 1942, 64, 2845–2849; cf. A., 1939, II, 370).—Fluorenene-1-carboxyl chloride (I) gives the amide (II), m.p. 226.5–227°, and thence (KOBz–KOH) 1-aminofluorenene, m.p. 118–118.5° (lit. 110°) (Ac, m.p. 138–138.3°, and Bz derivative, m.p. 149–149.8°), which afford by diazo-reactions 1-chloro-, m.p. 137–137.8°, 1-bromo- (III), m.p. 134–134.3° (lit. 135°), 1-iodo-, m.p. 146.5–147°, and 1-cyano-fluorenene (14%), m.p. 174–174.5° [also obtained (48%) (m.p. 177.2–177.8°) from (II) by PCl<sub>5</sub> at 200°; proof of orientation: hydrolysis by hot 50% H<sub>2</sub>SO<sub>4</sub> to the acid]. Fluorenene-4-carboxylic acid (prep. from diphenic acid by H<sub>2</sub>SO<sub>4</sub> at 140–150°) gives (SOCl<sub>2</sub>; aq. NH<sub>3</sub>) the amide, m.p. 223–224°, and thence (KOBz–KOH) 4-amino-, m.p. 138–139°, and (diazo-reaction) 4-bromo-fluorenene, m.p. 125–126° [depresses the m.p. of (III); cf. France *et al.*, A., 1938, II, 437; Miller *et al.*, A., 1936, 335]. The acid, m.p. 227–228°, obtained from 3:1:2-C<sub>6</sub>H<sub>3</sub>Br(CO)<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub> (Stephens, A., 1922, i, 141, m.p. 231.5°), is shown to be 3- (not 6-)bromo-2-benzoylbenzoic acid; it gives a *Me* ester, m.p. 136.7–137.5°, acid chloride, m.p. 121–122° (lit. 119–120°), amide, m.p. 202–202.5°, and thence 2-bromo-6-aminobenzophenone, m.p. 84.5–85.5°, which with NaNO<sub>2</sub>–H<sub>2</sub>SO<sub>4</sub> at 0° and later with added Na<sub>2</sub>SO<sub>4</sub> at 100° yields (III) (25%). Warm NH<sub>2</sub>Ph and (I) give fluorenoneanil-1-carboxylanilide, m.p. 184.7–185°. M.p. are on a Cu block.

R. S. C.

**Indene derivatives. II. Triketohydrindene.** A. Schönberg and R. Moubacher (J.C.S., 1943, 71–72).—Triketohydrindene (I), m.p. 255° (dark red solid melts to a bluish-green liquid, from which red crystals re-form), is obtained from its hydrate (ninhydrin) (II) and SOCl<sub>2</sub> at 60–70° (in a vac.), or less readily from (I) at 190° in a vac. (I) with hot H<sub>2</sub>O (1 min.) in absence of direct sunlight gives (II), also obtained when the bluish-green solution of (I) in C<sub>6</sub>H<sub>6</sub> is shaken with H<sub>2</sub>O. (I) gives a bluish-green solution in hot AcOH, but is almost colourless in cold AcOH owing to the formation of a dissociable additive compound. (II) heated in C<sub>6</sub>H<sub>6</sub> gives a bluish-green solution containing (I), and (II) at 190° in a current of O<sub>2</sub> yields *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O. An inner-salt formula is suggested for (II).

A. T. P.

**2-Nitro-1-amino-4-acylamidoanthraquinones.**—See B., 1943, II, 108.

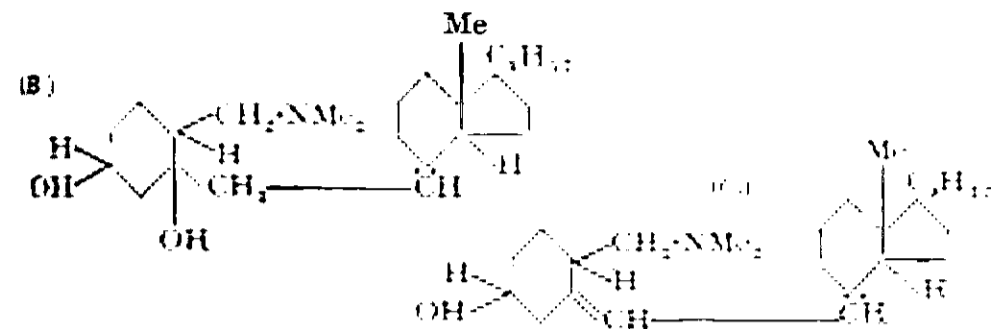
**Action of bases on 1-diazoanthraquinone-2-sulphonate and its derivatives.** J. I. Lynas-Gray and J. L. Simonsen (J.C.S., 1943, 45–47).—Na 1-diazoanthraquinone-2-sulphonate (I) (1 part), its 4-NHPh- (II) and 4-Br-derivative (III) in Et<sub>2</sub>O react with NH<sub>2</sub>R (3 parts) and Cu-bronze (0.003 part) at 0°, then at 60°, and the resulting mixtures are separated by chromatographic analysis (EtOH–Al<sub>2</sub>O<sub>3</sub>); yields of sulphonic acids are calc. as Na salts. (I) and NH<sub>2</sub>Ph thus give 1-aminoanthraquinone-2-sulphonic acid (IV) (100%), whereas (I) and aq. NH<sub>3</sub> (no Cu necessary) give (IV) (50%) and 1-hydroxyanthraquinone-2-sulphonic acid (50%). (I) and NH<sub>2</sub>Ph–AcOH at 0°, followed by aq. NaOH until alkaline, give the Na diazoamino-compound, which with aq. H<sub>2</sub>SO<sub>4</sub> at 50° affords PhOH, (IV), and the NH<sub>2</sub>Ph salt, m.p. 248° (darkens at 238°), of 1-diazo phenylaminoanthraquinone-2-sulphonic acid. (II) and NH<sub>2</sub>Ph yield 1-amino-4-anilinoanthraquinone-2-sulphonic acid (V) (15%) (*p*-toluidine salt, decomp. 269–270°, sinters 263°), 1-anilinoanthraquinone-3-sulphonic acid (VI) (45%) (Na salt; *p*-toluidine salt, decomp. ~290°, sinters 286–288°), and 1:4-dianilinoanthraquinone-2-sulphonic acid (VII) (40%) (Na salt; *p*-toluidine salt, decomp. 252°), whereas (II) and *p*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> or *m*-4-xylidine yield (V) (10 or 62%, respectively), (VI) (50 or 32%), and 4-anilino-1-*p*-toluidino- (40%) (Na salt; *p*-toluidine salt, m.p. 231–232°) or 4-anilino-1-*m*-4-xylidino-anthraquinone-2-sulphonic acid (6%) (Na salt; *p*-toluidine salt, decomp. 250°), respectively. Reduction of the respective Na sulphonates with glucose affords 1-anilino-4-*p*-toluidino-, m.p. 250°, and -4-*m*-4'-xylidino-anthraquinone, m.p. 232–233°, the latter also being obtained from 1:3:4-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>Cl, 1-amino-4-anilinoanthraquinone, Cu, and NaOAc. (III) and NH<sub>2</sub>Ph yield (V) (10%), 4-bromo-1-aminoanthraquinone-2-sulphonic acid (20%) (*p*-toluidine salt, decomp. 252°), (VI) (40%), and (VII) (30%), but (III) and aq. NH<sub>3</sub> at 70–80° give 1:4-diaminoanthraquinone-2-sulphonic acid (94%) (Na salt) and 5–6% of 4:4'-diamino-1:1'-dianthraquinolyl-3:3'-disulphonic acid (VIII) (Na<sub>2</sub> salt; *p*-toluidine salt, +3H<sub>2</sub>O, m.p. 234–235°), also obtained from Na 4-bromo-1-aminoanthraquinone-2-sulphonate and Cu–H<sub>2</sub>O (+ a drop of alkali), and reduced (glucose) to 4:4'-diamino-1:1'-dianthraquinonyl, m.p. 356–358° [? 3:3'-Br<sub>2</sub>-derivative, m.p. 415–416°, from (VIII) and Br]. (III) and NH<sub>2</sub>Me give 100% of Na 1-amino-4-methylaminoanthraquinone-2-sulphonate.

A. T. P.

#### IV.—STEROLS AND STEROID SAPOGENINS.

**Attempted synthesis of the antirachitic vitamin. XI. Partial synthesis of vitamin-D<sub>2</sub> and its 3-*epi*-compounds.** K. Dimroth and

E. Stockstrom (*Ber.*, 1942, 75, [B], 1263—1270).—The aldehyde (A), obtained according to Windaus *et al.* (A., 1943, II, 13; cf. Heilbron *et al.*, A., 1936, 1105) from vitamin-*D*<sub>2</sub> dinitrobenzoate, is converted by  $\text{Al}(\text{OPr}^\beta)_3$  in boiling  $\text{Pr}^\beta\text{OH}$  followed by  $\text{NaOH}$ - $\text{MeOH}$  into the corresponding primary alcohol (I), m.p. 71°, from which it is re-formed by oxidation with  $\text{CrO}_3$ . (I) is converted by  $\text{PBr}_3$  and  $\text{C}_5\text{H}_5\text{N}$  in  $\text{C}_6\text{H}_6$  followed by  $\text{Mg}$  in  $\text{Et}_2\text{O}$  into the Grignard reagent, which is treated with the base from 3-acetoxy-6-dimethylaminomethylcyclohexanone hydrochloride, m.p. 191°; the non-cryst. product is hydrolysed to isomeric alcohols (as B), m.p. 64° and 145°. Direct treatment of the acetate mixture with  $\text{PBr}_3$  followed by solid  $\text{KOH}$



gives the unsaturated alcohols (as C), m.p. 151° and 164°; the former is degraded (Hofmann) to vitamin-*D*<sub>2</sub> (I), m.p. 108—109° (block), 114° (bath),  $[\alpha]_D^{25} +122^\circ$  in  $\text{EtOH}$  [dinitrobenzoate, m.p. 148—149° (bath)], identical chemically and biologically with the natural product. The latter gives a substance (II), m.p. 179—180°, isomeric with (I) which is possibly feebly dextrorotatory. The ultra-violet absorption spectra of (I) and (II) are practically identical with one another and with that of natural (I). H. W.

Partial oxidation of cholic acid. T. F. Gallagher and W. P. Long (*J. Biol. Chem.*, 1943, 147, 131—134).—The OH groups of cholic acid are oxidised ( $\text{CrO}_3$ ) in the order 7, 12, 3. Me cholate and  $\text{CrO}_3$ -aq.  $\text{AcOH}$  at  $-7^\circ$  to  $0^\circ$  give products, separated chromatographically after acetylation into Me 7-keto-3:12-diacetoxycholanate (I) (40%), m.p. 114—117° (corr.),  $[\alpha]_D^{25} +64^\circ$  in  $\text{EtOH}$  [oxime, m.p. 155.5—157° (corr.)], Me 7:12-diketo-3-acetoxycholanate (40%), and Me dehydrocholate (20%). (I) and boiling aq.  $\text{NaOH}$ - $\text{EtOH}$  yield 3:12-dihydroxy-7-ketocholanic acid, m.p. 197—199° (corr.) (negligible rotation in  $\text{EtOH}$ ) (Me ester, m.p. 152—154°). The semicarbazone, m.p. 175—177° (corr.), of (I) and  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ - $\text{NaOEt}$ - $\text{EtOH}$  at 200° give a good yield of deoxycholic acid (cf. Haslewood, A., 1942, II, 365). A. T. P.

Preparation of progesterone by oxidising cholesterol with hydrogen peroxide. C. Serono and E. Marchetti (*Gazzetta*, 1942, 72, 151—154).—Cholesterol dibromide in  $\text{C}_6\text{H}_6$  with  $\text{H}_2\text{O}_2$  in presence of  $\text{Ag}_2\text{O}$  and dil.  $\text{NaOH}$ , at 60—80°, followed by debromination ( $\text{Zn}$ - $\text{AcOH}$ ), gives progesterone. E. W. W.

## V.—TERPENES AND TRITERPENOID SAPOGENINS.

Resistance of cineole derivatives to concentrated acids. G. Cusmano (*Gazzetta*, 1942, 72, 68—73).—2-Ketocineole (I) is fairly stable to conc.  $\text{HCl}$  (II), which slowly gives carvacrol and a product containing Cl; conc.  $\text{HNO}_3$  (III) has a slow oxidising action. (II) or (III) may be used to liberate 3-substituted 2-ketocineoles from their semicarbazones, since the velocity of hydrolysis is  $>$  that of formation of secondary products. (I) is stable to conc.  $\text{H}_2\text{SO}_4$  (IV) at  $0^\circ$ , but at  $5^\circ$  gives "isocamphorone." The semicarbazone of (I) with (IV) at  $<30^\circ$  slowly gives, by a new transposition, carvacrylsemicarbazide (V) (2-*p*-cymylsemicarbazide; cf. Wheeler *et al.*, A., 1929, 1438), with 8-hydroxycarvotanacetone (VI). Either of the two semicarbazones of carvone (VII) with (IV) gives (V) and (VI), with some (VII). The semicarbazone of (VI) gives (V) and (VI). E. W. W.

Decomposition of pernitrosocamphor. A. Gandini (*Gazzetta*, 1942, 72, 131—134).—Pernitrosocamphor in paraffin at 100° begins to lose  $\text{H}_2\text{O}$ . At 150—160° decomp. to  $\text{NO}$ ,  $\text{NO}_2$ , and  $\alpha$ -campholenitrile is soon complete. E. W. W.

Decomposition of ascaridole by heat. M. M. Janot and M. Chaigneau (*Compt. rend.*, 1942, 214, 746—747).—When ascaridole is heated in air or  $\text{N}_2$ , or at 320°/0.1 mm., it yields a mixture of  $\text{C}_3\text{H}_8$ ,  $\text{CO}$ ,  $\text{C}_3\text{H}_6$ , and  $\text{C}_2\text{H}_4$  in the approx. ratio 2:3:1:1, together with small amounts of  $\text{CO}_2$ . At 760 mm.  $\text{O}_2$  is unnecessary for the start of the decomp. J. N. A.

Melanthigenin and its identity with hederagenin. (Miss) Z. Mustafa and G. Soliman (*J.C.S.*, 1943, 70—71).—Melanthigenin,  $\text{C}_{30}\text{H}_{48}\text{O}_2 \cdot \text{CO}_2\text{H}$ , m.p.  $>325^\circ$ , isolated by hydrolysis of an  $\text{EtOH}$  extract of the defatted seeds of *Nigella sativa*, L., is hederagenin (comparison of the  $\text{Ac}_2$  and  $\text{Bz}_2$  derivatives and the Me ester and its  $\text{Ac}_2$  and  $\text{Bz}_2$  derivatives). The position of its one double bond is located by the formation of a diformyl lactone. F. R. S.

## VI.—HETEROCYCLIC.

Tetrahydrofurfuryl acetals.—See B., 1943, II, 113.

5-Hydroxycoumarins. I. Chalkones from 5-hydroxy-6-acetyl-4-methylcoumarin. N. M. Shah (*J. Univ. Bombay*, 1942, 11, A, Part 3, 109—112).—5-Hydroxy-6-acetyl-4-methylcoumarin (I) with  $\text{RCHO}$  and 50% aq.  $\text{KOH}$  (added slowly with cooling) at room temp. yields 5-hydroxy-4-methyl-6-coumarino styryl ketone (2 forms), m.p. 220—221° (II) and 175—176° (III), and 5-hydroxy-4-methyl-6-coumarino 3'-hydroxy-4'-methoxy-, m.p. 163—164°, 2':4'-dihydroxy-, m.p. 166—167°, 3':4'-dihydroxy-, m.p. 163°, 4'-methoxy-, m.p. 243°, and 2'-hydroxy-styryl ketone, m.p. 233° (decomp.). With dil.  $\text{NaOH}$  at 100°, (II) gives (III), whilst (III) yields 4-methylflavono-7':8':6:5- $\alpha$ -pyrone, m.p. 237°. With  $\text{SeO}_2$  in  $\text{C}_5\text{H}_5\text{N}$ - $\text{OH}$ , (III) yields 4-methylflavono-7':8':6:5- $\alpha$ -pyrone.  $\text{CHPh} \cdot \text{CH} \cdot \text{CHO}$  gives no cryst. product with (I). A. Li.

Aluminium chloride, new reagent for condensation of  $\beta$ -ketonic esters with phenols. VII. Condensation of resacyl- and gallacyl-phenones (4-acyl-resorcinol and -pyrogallols) containing long-chain acyl groups. M. C. Chudgar and N. M. Shah (*J. Univ. Bombay*, 1942, 11, A, Part 3, 113—115).—4-Stearylresorcinol (I) and  $\text{CH}_2\text{Ac} \cdot \text{CO}_2\text{Et}$  with  $\text{AlCl}_3$  in  $\text{PhNO}_2$  at 110—115° yields 5-hydroxy-6-stearyl-4-methylcoumarin (+0.5 $\text{H}_2\text{O}$ ), m.p. 116—117° (red colour with  $\text{FeCl}_3$ ; acetate, m.p. 98°), which with  $\text{NaOAc}$  in  $\text{Ac}_2\text{O}$  gives 2':4'-dimethyl-3'-hexadecylchromono-7':8':6:5- $\alpha$ -pyrone, m.p. 135—136°. (I) is reduced (Clemmensen) to 4-octadecylresorcinol, which with  $\text{CH}_2\text{Ac} \cdot \text{CO}_2\text{Et}$  ( $\text{POCl}_3$ ) at room temp. yields 7-hydroxy-6-octadecyl-4-methylcoumarin, m.p. 116—117° (acetate, m.p. 78—79°). 5-Nitro- and 5-bromo-4-stearylresorcinol and 4-stearylpyrogallol do not undergo this reaction. These results are explained in terms of fixation of the double linking. A. Li.

Reduction of  $-\text{CH}(\text{OH}) \cdot \text{CCl}_3$  group attached to benzo- $\alpha$ -pyrone nucleus. II. M. C. Chudgar and N. M. Shah (*J. Univ. Bombay*, 1942, 11, A, Part 3, 116—119).—7-Methoxy-4-methyl-3- $\beta\beta\beta$ -trichloro- $\alpha$ -methoxyethylcoumarin is reduced ( $\text{Zn}$ - $\text{AcOH}$ ) to 7-methoxy-4-methyl-3- $\alpha$ -chlorovinyl-, m.p. 160—161°, or ( $\text{Zn}$ - $\text{AcOH}$ -conc.  $\text{HCl}$ ) to 3- $\beta\beta$ -dichloroethylcoumarin, m.p. 113—114°. 7-Hydroxy-4-methyl-6-ethyl-3- $\beta\beta\beta$ -trichloro- $\alpha$ -hydroxyethyl- (I) is reduced ( $\text{Zn}$ - $\text{AcOH}$ ) to 3- $\alpha$ -chlorovinyl-, m.p. 138—140° (acetate, m.p. 191—192°), or ( $\text{Zn}$ - $\text{AcOH}$ - $\text{HCl}$ ) to 3- $\beta\beta$ -dichloroethylcoumarin, m.p. 253—255° [acetate (II), m.p. 167°], similarly obtained from the acetate of (I). The latter is reduced ( $\text{Zn}$ - $\text{AcOH}$ ) to (II). 4-Butylresorcinol with  $\text{CO}_2\text{Et} \cdot \text{CHAc} \cdot \text{CH}(\text{OH}) \cdot \text{CCl}_3$  and  $\text{POCl}_3$  at room temp. yields 7-hydroxy-4-methyl-3- $\beta\beta\beta$ -trichloro- $\alpha$ -hydroxyethyl-6-butylcoumarin, m.p. 166—167° (acetate, m.p. 123—124°), which undergoes the same reactions as (I), giving 7-hydroxy-, m.p. 167°, and -acetoxy-4-methyl-3- $\alpha$ -chlorovinyl-6-butyl-, m.p. 143°, and 7-hydroxy-, m.p. 196—197°, and -acetoxy-4-methyl-3- $\beta\beta$ -dichloroethyl-6-butylcoumarin, m.p. 156—157°. A. Li.

Transformation of *o*-nitrobenzoyloxyacetophenones into *o*-hydroxyaroylnitrobenzoylmethanes, and synthesis of nitroflavones. V. V. Virkar (*J. Univ. Bombay*, 1942, 11, A, Part 3, 136—139; cf. A., 1940, II, 22).—*o*-3'-Nitrobenzoyloxyacetophenone, m.p. 99—100° (from *o*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{COMe}$  and *m*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$  in  $\text{C}_5\text{H}_5\text{N}$  at 100°), with  $\text{Na}$  in  $\text{PhMe}$  at 130° yields 3'-nitro-2-hydroxydibenzoylmethane, m.p. 157°, cyclised ( $\text{HBr}$ - $\text{AcOH}$ ) to 3'-nitro-, m.p. 203°, reduced ( $\text{SnCl}_2$ - $\text{Sn}$ - $\text{HCl}$ ) to 3'-amino-flavone. Similarly 1-3', m.p. 152°, and 1-4'-nitrobenzoyloxy-2-acetonaphthone, m.p. 151°, yield respectively 1-hydroxy-3'-, m.p. 196°, and -4'-nitrobenzoyl-2'-naphthoylmethane, m.p. 222°, 3'-, m.p. 262°, and 4'-nitro-, m.p. 293°, and 3'-, m.p.  $>300^\circ$  (hydrochloride, m.p.  $>300^\circ$ ), and 4'-amino-flavone, m.p. 265° (hydrochloride, m.p.  $>300^\circ$ ). A. Li.

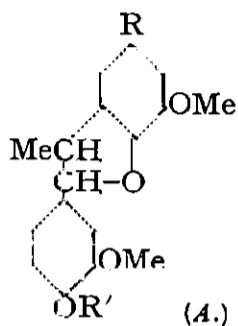
Chromones of the naphthalene series. Transformation of *o*-naphthoyloxyacetophenones into *o*-hydroxydiaroylmethanes. V. V. Virkar and R. C. Shah (*J. Univ. Bombay*, 1942, 11, A, Part 3, 140—143; cf. A., 1940, II, 22).—*o*- $\alpha$ -, m.p. 108°, and *o*- $\beta$ -naphthoyloxyacetophenone, m.p. 119° (from *o*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{COMe}$  and  $\text{C}_{10}\text{H}_7 \cdot \text{COCl}$  in  $\text{C}_5\text{H}_5\text{N}$ ), with  $\text{Na}$  in  $\text{PhMe}$  at 130° yield respectively *o*-hydroxybenzoyl-1'-, m.p. 124°, and -2'-naphthoylmethane, m.p. 141°, cyclised by  $\text{HI}$  in  $\text{Ac}_2\text{O}$  to 2-1'-, m.p. 138—139°, and 2-2'-naphthylchromone, m.p. 134°. Similarly 4-benzoyloxy-2-2'-naphthoyloxyacetophenone, m.p. 103—104°, gives 2-hydroxy-4-benzoyloxybenzoyl-2'-naphthoylmethane, m.p. 167—168°, which yields, with  $\text{HBr}$  in  $\text{AcOH}$ , 7-benzoyloxy-, m.p. 198°, and with  $\text{HI}$  in  $\text{Ac}_2\text{O}$ , 7-hydroxy-2-2'-naphthylchromone, m.p. 288° (acetate, m.p. 190°), whilst 2-benzoyloxy-4-methoxyacetophenone gives 2-hydroxy-4-methoxydibenzoylmethane, m.p. 105°, and 7-methoxyflavone. 4-Benzoyloxy-2-1'-naphthoyloxyacetophenone, m.p. 104°, with  $\text{Na}$  in boiling  $\text{C}_6\text{H}_6$  yields 7-hydroxy-2-1'-naphthylchromone, m.p. 291° (sintering at 188°) (acetate, m.p. 173°; benzoate, m.p. 159°). A. Li.

Kostanecki-Robinson reaction. IV. Acetylation, propionylation, and butyrylation of oreopropiophenone. P. L. Trivedi, S. M. Sethna, and R. C. Shah (*J. Univ. Bombay*, 1942, 11, A, Part 3, 144—150).—2:4-Dihydroxy-6-methylpropiophenone (I), m.p. 127—128° (from orcinol,  $\text{EtCN}$ ,  $\text{ZnCl}_2$ , and  $\text{HCl}$  in  $\text{Et}_2\text{O}$ ), with  $\text{NaOAc}$  in  $\text{Ac}_2\text{O}$  at 180—190° yields the acetate, m.p. 122—123°, of 7-hydroxy-2:3:5-

*trimethylchromone*, m.p. 269—273°, the *Me ether*, m.p. 159°, of which is also obtained by treatment of 2:4:6:1-(OMe)<sub>4</sub>C<sub>6</sub>H<sub>2</sub>Me·COMe (II) with EtOAc and Na at 115—120°, methylation (MeI in COMe<sub>2</sub>), and cyclisation (HBr at room temp.). (I) with EtCO<sub>2</sub>Na and (EtCO)<sub>2</sub>O at 180—190° yields the *propionate*, m.p. 75°, of 7-hydroxy-3:5-dimethyl-2-ethylchromone, m.p. 258—261° (acetate, m.p. 107—108°), the *Me ether*, m.p. 130—131°, of which is also obtained from (II) by treatment with EtCO<sub>2</sub>Et and Na at 115—120°, methylation, and cyclisation. (I) with PrCO<sub>2</sub>Na and (PrCO)<sub>2</sub>O at 180—190° yields a product which with conc. H<sub>2</sub>SO<sub>4</sub> gives 7-hydroxy-3:5-dimethyl-2-propylchromone, m.p. 238—241° (acetate, m.p. 95°), the *Me ether*, m.p. 91—92°, of which is also obtained from (II), PrCO<sub>2</sub>Et, and Na as above. A. Li.

**Dibenzfurans.**—See B., 1943, II, 6.

**Lignin. LII. Constitution of dehydrodiisoeugenol and its significance in the chemistry of lignin.** K. Freudenberg and H. Richtzenhain (*Annalen*, 1942, **552**, 126—135; cf. Erdtmann, A., 1933, 390, 818).—Evidence is adduced in favour of the constitution (A) (R = CH<sub>2</sub>CHMe, R' = H) for dehydrodiisoeugenol. Fission of the compound A (R = Pr<sup>n</sup>, R' = Me) with K in liquid NH<sub>3</sub> followed by methylation (NaOH-Me<sub>2</sub>SO<sub>4</sub>) of the product gives α-3:4-dimethoxyphenyl-β-2:3-dimethoxy-5-propylphenylpropane (I), b.p. 145—150°/0.01 mm., demethylated by HBr in boiling AcOH to the corresponding (OH)<sub>4</sub>-compound (II), m.p. 131°. 2-Hydroxy-3-methoxy-5-allyl- is hydrogenated (Pd-BaSO<sub>4</sub> in AcOH) to 2-hydroxy-3-methoxy-5-n-propyl-benzaldehyde, b.p. 155°/10 mm.



(A.)

(2:4-dinitrophenylhydrazones, m.p. 223°), the Na salt of which is methylated (NaOH-Me<sub>2</sub>SO<sub>4</sub>) to 2:3-dimethoxy-5-n-propylbenzaldehyde, b.p. 155—156°/10 mm. (2:4-dinitrophenylhydrazones, m.p. 202°). This is converted by hippuric acid, anhyd. NaOAc, and Ac<sub>2</sub>O at 100° into the *azlactone*, C<sub>21</sub>H<sub>21</sub>O<sub>4</sub>N, m.p. 158—159°, hydrolysed by boiling 10% NaOH to 2:3-dimethoxy-5-n-propylphenylpyruvic acid, m.p. 130—131°, which is oxidised by H<sub>2</sub>O<sub>2</sub> in presence of NaHCO<sub>3</sub> at 0° to 2:3-dimethoxy-5-n-propylphenylacetic acid, m.p. 93—94°. This is converted into the chloride, which with veratrole and AlCl<sub>3</sub> in CS<sub>2</sub> affords 2:3-dimethoxy-5-n-propylbenzyl 3:4-dimethoxyphenyl ketone, m.p. 87—88°. The ketone is converted into its Na<sub>4</sub> derivative, which with MeI in C<sub>6</sub>H<sub>6</sub> at 100° yields α-keto-α-3:4-dimethoxyphenyl-β-2:3-dimethoxy-5-n-propylphenylpropane, m.p. 101°, slowly reduced (Clemmensen) to (I), which is hydrolysed to (II). Attempted dehydrogenation of coniferyl alcohol (III) by FeCl<sub>3</sub> leads to an amorphous condensate which after methylation, treatment with hot alkali, renewed methylation, and oxidation yields veratric acid with traces of isohemipinic acid. These acids are obtained from lignin and the coumaronecarboxylic acid (A; R = CO<sub>2</sub>H, R' = Me) under the same circumstances. Dehydrogenation of (III) is therefore in part at any rate similar to that of isoeugenol. H. W.

**Furylchromones.** G. B. Marini-Bettolo (*Gazzetta*, 1941, **71**, 635—641).—2-Hydroxy-4-methoxy- (I) and -3:4-dimethoxy-ω-furfurylideneacetophenone (II) with SeO<sub>2</sub> in boiling C<sub>6</sub>H<sub>11</sub>·OH (15 hr.) give 7-methoxy-, m.p. 160°, and 7:8-dimethoxy-2-furylchromone, m.p. 165°. 2:4:5:1-OH·C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>·COMe with furfuraldehyde and KOH-EtOH gives 2-hydroxy-4:5-dimethoxy-ω-furfurylideneacetophenone (III), m.p. 128°, which with SeO<sub>2</sub> gives 6:7-dimethoxy-2-furylchromone, m.p. 204°. With hot EtOH-KOH, followed by H<sub>2</sub>O<sub>2</sub>, (I), (II), and (III) give respectively 3-hydroxy-7-methoxy-, m.p. 178°, -7:8-dimethoxy-, m.p. 244°, and -6:7-dimethoxy-2-furylchromone, m.p. 212°. With dil. HCl in boiling EtOH (30 hr.), (I), (II), and (III) give respectively 2-hydroxy-4-methoxy-, m.p. 165°, -3:4-dimethoxy-, m.p. 98°, and -4:5-dimethoxy-phenacyl-lævulic acid, m.p. 127, furylchromanones not being formed. E. W. W.

**Arylthioisatins.**—See B., 1943, II, 109.

**Thionaphthen vat dye.**—See B., 1942, II, 47.

**Phenoxthionins.**—See B., 1943, II, 109.

**Oxides of phenoxthionins.**—See B., 1943, II, 45.

**Synthesis of vitamin-B<sub>6</sub>.**—See B., 1943, III, 21.

**Nicotin-p-phenetide.**—See B., 1943, III, 41.

**Oxidation of adrenaline.** F. Bergel and A. L. Morrison (*J.C.S.*, 1943, 48).—Adrenaline (I) in 2% AcOH is oxidised (KIO<sub>3</sub>) to an iodoquinone (II), which is reduced (NaHSO<sub>3</sub>) and acetylated to 2-iodo-5:6-diacetoxy-1-methylindole, m.p. 153—155°. Reduction of (II) with Zn-Ac<sub>2</sub>O-NaOAc or Mg-AcOH affords 5:6-diacetoxy-1-methylindole (III), m.p. 100—101°. Catalytic oxidation (Pd-C) of (I) causes 2 O<sub>2</sub> to be absorbed, and although (II) cannot be isolated, reduction catalytically or with NaHSO<sub>3</sub> gives a substance apparently identical with (III). F. R. S.

**5-Hydroxyindole.** F. Bergel and A. L. Morrison (*J.C.S.*, 1943, 49).—2-Nitro-5-benzyloxytoluene, m.p. 70—71°, prepared from the OH-compound, with KOEt and Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> gives 2-nitro-5-benzyloxy-pyruvic acid, m.p. ~100—105° (phenylhydrazone, m.p. 152—153°),

which is reduced (FeSO<sub>4</sub>-aq. NH<sub>3</sub>) to 5-benzyloxyindole-2-carboxylic acid, m.p. 193—194° (*Me ester*, m.p. 150—151°). Reduction (Pd-C-MeOH-H<sub>2</sub>) of the acid affords 5-hydroxyindole-2-carboxylic acid, m.p. 246° (decomp.) (*Me ester*, m.p. 146—147°), which is decarboxylated (Cu) in small yield to 5-hydroxyindole, m.p. 107—109°. F. R. S.

**Mechanism of indole formation from phenacylarylamines. I.** A. F. Crowther, F. G. Mann, and (in part) D. Purdie (*J.C.S.*, 1943, 58—68).—The conversion of the phenacyl derivatives of primary arylamines into 2-arylindoles depends on the presence of catalytic impurities (e.g., amine hydrobromides and hydriodides). The theory of the mechanism that the derivative undergoes normal cyclisation to give 3-phenylindole which isomerises to the 2-compound is incorrect since pure phenacylaniline (I) is stable but when heated with traces of many hydrobromides and hydriodides and quaternary bromides and iodides is converted readily into 2-phenylindole (II). The catalysts are listed according to whether they cause conversion into (II), cause partial conversion into diphenylacylaniline, no apparent change, or decomp. to non-cryst. syrups. The alternative theory that a diamine is first formed and cyclises with loss of the original amine is also incorrect. Pure (I) and NH<sub>2</sub>Ph give NN-di-(β-anilino-α-phenylvinyl)aniline (III), m.p. 205—209°, but in presence of NH<sub>2</sub>Ph.HBr, (II) is obtained. Pure (I) and p-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> yield NN-di-(β-p-tolylamino-α-phenylvinyl)-p-toluidine, m.p. 175—183°, and with a catalyst, 2-phenyl-5-methylindole is obtained. Similarly (I), 2:4:1-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>·NH<sub>2</sub>, and NH<sub>2</sub>Ph.HBr form 2-phenyl-5:7-dimethylindole, isolated as the *picrate*, m.p. 156—157.5°. The following are described: *hydrobromide*, m.p. 183° (decomp.), and *hydriodide*, m.p. 145°, of (I), p-chlorophenacylaniline, m.p. 113—115° (*Ac derivative*, m.p. 143°), and di-(β-anilino-α-p-chlorophenylvinyl) ether, m.p. 192—193° (*Ac<sub>2</sub> derivative*, m.p. 232—233°), obtained at the same time; p-chlorophenacyl-p-toluidine, m.p. 148—150°, and -2:4-dimethylaniline, m.p. 117°; 2-p-chlorophenyl-5-methylindole, m.p. 250.5—251.5° [*NO-derivative*, m.p. 277° (decomp.)]; p-toluenesulphonyl derivative, m.p. 71°, of N-ethyl-p-toluidine; 2:4-dimethyl-, b.p. 229—232°/763 mm., and p-chloro-N-ethylaniline, b.p. 247—250°/760 mm. (p-toluenesulphonyl derivative, m.p. 102.5—104°); 4:4'-diethoxydiphenylamine, m.p. 94°; *hydrochloride*, m.p. 158°, and *picrate*, m.p. 110°, of phenacyl-N-ethylaniline; phenacyl-N-ethyl-p-toluidine, m.p. 110—111°; p-chlorophenacyl-N-ethylaniline, m.p. 83° (*hydrochloride*, m.p. 169°; *picrate*, m.p. 116—117°), -N-isobutylaniline, m.p. 91°, and -N-ethyl-p-toluidine (IV), m.p. 95.5° [*hydrochloride*, m.p. 177—178° (decomp.)]; *picrate*, m.p. 135—136°]; and p-chloro-(p'-chlorophenacyl)-N-ethylaniline, m.p. 105—106°.

The phenacyl derivatives of *sec.* arylalkylamines behave entirely differently, giving 3-aryl-1-alkylindoles, which (with one exception) could not be isomerised to 2-aryl-1-alkylindoles. When (IV) is exposed to air at 100° for 7 hr., appreciable amounts of p-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H are obtained, and with EtOH-ZnCl<sub>2</sub> or fused with ZnCl<sub>2</sub> it gives 3-p-chlorophenyl-5-methyl-1-ethylindole (V), m.p. 92° (*picrate*, m.p. 102.5—103.5°), and some *dimeride*, m.p. 157.5°. Similarly, 3-phenyl-1-ethyl-, b.p. 188—192°/1.5 mm. (*picrate*, m.p. 83—83.5°), and -5-methyl-1-ethyl-indole, b.p. 220—222°/17 mm. (*picrate*, m.p. 107.5—108°), and 3-p-chlorophenyl-1-methyl-, m.p. 96° (*picrate*, m.p. 107—107.5°), -1-ethyl-, m.p. 81°, and -1-isobutyl-indole, m.p. 71—72°, are obtained, but phenacyl-N-methylaniline with EtOH-ZnCl<sub>2</sub> gives 3-phenyl-1-methylindole and with fused ZnCl<sub>2</sub> the 2Ph derivative. Phenacyl-N-ethylaniline and NH<sub>2</sub>Ph at 150° for 8 hr. afford NHPHt and (III), whilst (IV) similarly yields p-chlorophenacylaniline and NN-di-(β-anilino-α-p-chlorophenylvinyl)aniline, m.p. 172—180°. p-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>Et and (IV) (equimols.) in air at 100° for 7 hr. give much p-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H and 4:4'-dichlorobenzil but in a closed vessel at 140—150°, p-chloro-(αβ-bis-p-tolylethylamino)-vinylbenzene, m.p. 123—123.5°, is formed in addition; the latter is the only diamine obtained and it could not be converted into an indole. When (IV) is boiled with excess of NHPHt, NHPHtBu<sup>β</sup>, or p-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>Et, (V) is obtained in each case. An ionic mechanism is put forward to explain the results obtained. The following are also described: p-chlorophenyl-N-ethylnitrosoamine, m.p. 58—59°; p-chloroacetophenonephenylhydrazones, m.p. 112—113°; 2-phenyl-, m.p. 84—84.5° (3-NO-derivative, m.p. 130—131°), 2-phenyl-5-methyl-, b.p. 171—173°/0.2 mm., m.p. 70.5° (3-NO-derivative, m.p. 161—162°), and 2-p-chlorophenyl-1-ethylindole, b.p. 171°/0.2 mm., m.p. 86—87° (3-NO-derivative, m.p. 138—139°); 2-p-chlorophenyl-1-n-propylindole, b.p. 222—225°/15 mm., m.p. 54° (3-NO-derivative, m.p. 137—138°), -1-isobutylindole, b.p. 173—178°/0.3 mm., m.p. 87—87.5° (3-NO-derivative, m.p. 93°), and -5-methyl-1-ethylindole, b.p. 239°/13 mm., m.p. 127—128.5°. The crystallographic measurements of the dimeride of (V) are given. F. R. S.

**3-Substituted indoles.**—See B., 1943, II, 109.

**8-Aminoquinaldone.** G. Jacini (*Gazzetta*, 1942, **72**, 42—46).—o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> (1 mol.) and CHAc·CO<sub>2</sub>Et (I) (2 mols.) (room temp.) give 2-methylbenzimidazole and some Et<sub>2</sub> o-phenylenebis-β-amino-crotonate, m.p. 103°, which in paraffin (II) at 200—250° gives a substance, C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>N<sub>2</sub>, decomp. ~350°. o-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NHAc and (I) in boiling EtOH give Et β-o-acetamidoanilinocrotonate, m.p. 104°, which in (II) at 230—240° gives 8-acetamido-4-hydroxy-2-methyl-

quinoline, m.p. 292—293°. This with boiling 10%  $\text{H}_2\text{SO}_4$  gives 8-amino-4-hydroxy-2-methylquinoline, decomp.  $\sim 300^\circ$ . E. W. W.

**Preparation of 2-hydroxy-4-alkylquinoline-6-sulphonamides.** (Signa, L. Monti and S. Palmieri (*Gazzetta*, 1941, 71, 662—667).— $\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\text{Ac}$  and  $\text{SO}_2\text{Cl}_2$  at  $80^\circ$  give a product which with conc. aq.  $\text{NH}_3$  gives 2-hydroxy-4-methylquinoline-6-sulphonamide (I), m.p. 316—318° (softens at  $310^\circ$ ), also obtained from the quinoline. [The  $\text{SO}_2\text{Cl}_2$  must be freshly distilled, otherwise the product includes  $p\text{-NH}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Ac}$  (also obtained, prep. modified, from  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  and  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ ), which does not condense to (I), either in conc.  $\text{H}_2\text{SO}_4$  or in heavy petroleum at  $300^\circ$ .] *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Ac}$  similarly treated give 2-hydroxy-4 : 8-, m.p. 310—312° (decomp.), and -4 : 7-dimethylquinoline-6-sulphonamide, m.p. 325—326° (decomp.), and 2-hydroxy-4 : 6-dimethylquinoline, respectively. E. W. W.

**Quinolines, benzquinolines, and acridines.**—See B., 1943, II, 6.

**Mechanism of cyclisation reactions.** E. Berliner (*J. Amer. Chem. Soc.*, 1942, 64, 2894—2898).—Ring-closure by acid of  $o\text{-CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{COR}$  to 9-substituted anthracenes, of  $o\text{-NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{COR}$  to 5-substituted acridines, etc. has, as first step, addition of a proton to give  $o\text{-CH}_2\text{Ph}^+\cdot\text{C}_6\text{H}_4\cdot\text{C}^+\text{R}\cdot\text{OH}$  etc., which then closes the ring by electrophilic attack on the Ph marked \*. Acid ring-closure of  $\text{CAR}_3\cdot\text{OH}$  to 9-arylfluorenones occurs by preliminary formation of  $^+\text{CAR}_3$ , which is evidenced by development of colour similar to that of the carbinol in conc.  $\text{H}_2\text{SO}_4$ . *o*- $\alpha$ -, m.p. 96.4—97.2°, and *o*- $\beta$ -naphthylaminoacetophenone (I) [both prepared from  $\text{C}_{10}\text{H}_7\text{Br}$ ,  $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$  (II),  $\text{K}_2\text{CO}_3$ , and Cu powder in boiling  $\text{PhNO}_2$ ], b.p. 195—196°/6 mm., with a little  $\text{H}_2\text{SO}_4$  in AcOH at  $100^\circ$  give rapidly 5-methyl-1 : 2-, m.p. 111.6—112.2° [sulphate; picrate, m.p. 251—255° (decomp.)], and -3 : 4-benzacridine, m.p. 145—145.2° [picrate, m.p. 245—248° (decomp.)], obtained also from (I) by boiling with picric acid. Condensing 9-bromophenanthrene with (II) as above and heating the product with  $\text{H}_2\text{SO}_4$ -AcOH gives 5-methyl-1 : 2 : 3 : 4-dibenzacridine, m.p. 121.4—122.4° [picrate, m.p. 206—208° (decomp.)]. 2- $\text{C}_{10}\text{H}_7\cdot\text{COPh}$  [prep. from 2- $\text{C}_{10}\text{H}_7\cdot\text{CN}$  by  $\text{MgPhBr}\cdot\text{Et}_2\text{O}$  and then  $\text{HCl}\cdot\text{H}_2\text{O}\cdot\text{COMe}_2$  (later with  $\text{C}_6\text{H}_6$ ); 82.5% yield], m.p. 81—82°, and  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$  in  $\text{Et}_2\text{O}$  give, after decomp. by aq.  $\text{NH}_4\text{Cl}$ , phenyl- $\alpha$ -naphthyl- $\beta$ -naphthylcarbinol (III), m.p. 168—169°, and  $+\text{x}\cdot\text{C}_6\text{H}_5$  or  $\text{x}\cdot\text{EtOH}$ , m.p. 195—205°, which with a few drops of  $\text{HCl}$  in boiling AcOH gives a green and then a red colour, 9-phenyl-1 : 2 : 5 : 6-dibenzfluorene (IV), m.p. 219—219.5°, being formed during the second change; (III) gives a green ppt. with  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ , I,  $\text{PCl}_5$ , or  $\text{SnCl}_4$  in  $\text{C}_6\text{H}_6$  and (IV) is formed after  $\sim 5$  min. at  $100^\circ$ . Phenyl-di- $\alpha$ , m.p. 169—170°, and  $\beta$ -naphthylcarbinol (similarly prepared), m.p. 216.5—217.5°, give similarly 9-phenyl-3 : 4 : 5 : 6-, m.p. 275°, and -1 : 2 : 7 : 8-dibenzfluorene, m.p. 148.5—149.5°, respectively.  $o\text{-C}_6\text{H}_4\text{Ph}\cdot\text{COPh}$  with 34% aq.  $\text{HBr}$  + AcOH at the b.p. gives 9-phenylfluorenyl acetate and the polymeride (V) of 9-fluorenyl and with a little  $\text{H}_2\text{SO}_4$  in  $\text{Ac}_2\text{O}$  at  $100^\circ$  gives mainly (V). M.p. are corr. R. S. C.

**Sulphonamide derivatives of pyrazole.** I. 1-*p*-Sulphonamidophenyl-3-methyl-5-pyrazolone. G. B. Crippa and S. Maffei (*Gazzetta*, 1942, 72, 97—99).— $p\text{-NH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$  diazotised and reduced gives *p*-hydrazinobenzenesulphonamide, m.p. 155° (Ac derivative, m.p. 224°), which with  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  (I) gives the sulphonamidophenylhydrazone (II), m.p. 142°, of (I). Above its m.p., (II) gives 1-*p*-sulphonamidophenyl-3-methyl-5-pyrazolone, m.p. 237°. E. W. W.

**Action of copper on ethyl malonate and on 5 : 5-diethylbarbituric acid [exposed to the air].** B. Ciocca and E. Dumontel (*Gazzetta*, 1942, 72, 197—200).— $\text{CH}_2(\text{CO}_2\text{Et})_2$  (I) exposed to the air with Cu powder at 50—60° gives its Cu derivative,  $\text{C}_7\text{H}_{11}\text{O}_4\text{Cu}$ . (I) does not react with CuO or  $\text{Cu}_2\text{O}$ . 5 : 5-Diethylbarbituric acid in EtOH similarly gives a Cu derivative,  $\text{C}_7\text{H}_{10}\text{O}_3\text{N}_2\text{Cu}_2$ . E. W. W.

**cycloHeptenylbarbituric acids.**—See B., 1940, III, 42.

**Barbituric acids.**—See B., 1943, III, 89.

**Pyrimidines.**—See B., 1943, II, 109.

**Sulphanilamidopyrimidines.**—See B., 1943, II, 21.

**Thioammelines.**—See B., 1943, II, 130.

**Indigoid dyes of the cis-series.** II. *NN'*-Ethyleneindigotin. R. Pummerer and E. Stieglitz (*Ber.*, 1942, 75, [B], 1072—1085).—Dehydroindigotin (I) and furylethylene in dry  $\text{PhCl}$  at  $\sim 100^\circ$  yield *NN'*-furylethyleneindigotin, m.p. 213°. Similarly (I) and  $\text{CH}_2\text{CH}\cdot\text{CO}_2\text{Me}$  in a sealed tube at  $\sim 100^\circ$  afford *Me indigotin*-*NN'*-acrylate, m.p. 209°, hydrolysed by  $\text{NaHCO}_3$  in boiling aq. MeOH to indigotin-*NN'*-acrylic acid (Ag and Na salts), decarboxylated by Cu powder in boiling  $\text{PhCl}$  under  $\text{CO}_2$  to *NN'*-ethyleneindigotin ( $\text{C}_8\text{H}_4\text{N}_2\text{CH}_2$ )<sub>2</sub> (II). This is converted by boiling  $\text{KOH}\cdot\text{EtOH}\cdot\text{H}_2\text{O}$  into ethyleneindigotin-yellow,  $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_2\cdot 0.5\text{H}_2\text{O}$ . The structure of (II) is established by its oxidation (conc.  $\text{HNO}_3$  in AcOH) to ethylenedi-isatin, m.p. 279°, transformed by  $\text{NaOH}$  and  $\text{H}_2\text{O}_2$  into ethylenedianthranilic acid, m.p. 228°. The experiments do not lead to a particular formula or theory to explain the play of

colours of alkyleneindigotins (III) in various solvents but show that it is due to mesomerism since (a) it cannot be due to *cis-trans*-isomerism because the *trans*-forms of (III) are spatially impossible, (b) there cannot be a mixture of two isomerides of other type or tautomerides as no evidence therefor can be found in the absorption curves of the extreme red and blue solutions, (c) association to double mols. is not causative of the blue solutions, and (d) a little dipole solvent is required to cause much displacement towards blue whereas much more of a different solvent is required to produce the reverse effect. H. W.

**Absorption spectra of phthalocyclohydrazides.**—See A., 1943, I, 80.

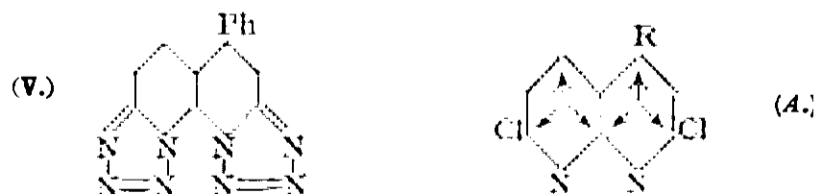
**Quinazoline derivatives.** I. L. Monti and A. Simonetti. II. L. Monti, A. Osti, and S. Piras. III. L. Monti (*Gazzetta*, 1941, 71, 651—653, 654—658, 658—662).—I. 4-Hydroxy-2-methylquinazoline (I) heated with  $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , with furfuraldehyde, and with chloral, gives respectively 4-hydroxy-2-*p*-dimethylaminostyryl-, m.p. 300—302° (decomp. from  $290^\circ$ ) (picrate, m.p. 214—215°), -2- $\beta$ -furyl-vinyl-, m.p. 210—212° (darkening 206—208°) (picrate, decomp. 224—226°), and -2- $\gamma\gamma\gamma$ -trichloropropenyl-quinazoline, decomp. 194—195°.

II. 4-Hydroxyquinazoline (II) and  $\text{NHBz}\cdot\text{CH}_2\cdot\text{OH}$  (III) in boiling AcOH give 3-benzamidomethyl-4-quinazoline, m.p. 180—182°, hydrolysed by boiling dil.  $\text{HCl}$  to the dihydrochloride, m.p. 242—244°, of 3-aminomethyl-4-quinazoline (IV) [picrate, m.p. 200—202° (decomp. from  $180^\circ$ )]. Similarly (I) and (III) in AcOH give 2-methyl-3-benzamidomethyl-4-quinazoline, m.p. 184—186°, hydrolysed by dil.  $\text{HCl}$ , followed by dil. aq.  $\text{NH}_3$ , to 2-methyl-3-aminomethyl-4-quinazoline (V), m.p. 268—270° (decomp.; darkening from 235—240°) [picrate, m.p. 210—240° (decomp.)]. The structure assigned to (IV) and (V) is supported by the non-reactivity of 3-methyl- and 2 : 3-dimethyl-quinazoline [prepared by  $\text{Me}_2\text{SO}_4$ -methylation of (II) and (I), respectively] with (III).

III. In petroleum jelly at  $180^\circ$ , (I),  $\text{NH}_4\text{Cl}$ , and paraformaldehyde give (V). Using  $\text{NH}_2\text{Me}_2\text{Cl}$ ,  $\text{NH}_2\text{Et}_2\text{Cl}$ , and piperidine hydrochloride, 2-methyl-3-dimethylaminomethyl-, m.p. 295—296° (darkening  $280^\circ$ ) (picrate\*, darkens  $250^\circ$ ), -3-diethylaminomethyl-, m.p. 282—284° (darkening  $250^\circ$ ) (picrate\*, darkens 220—225°), and -3-piperidinomethyl-4-quinazoline, decomp. 288—290° (darkening  $270^\circ$ ) (picrate\*, darkens 205—210°) are formed. (\* These picrates carbonise without melting.) E. W. W.

**Naphthyridines.** I. Derivatives of 4-phenyl-1 : 8-naphthyridine. II. Reactivity of 2 : 7-dichloro-4-phenyl-1 : 8-naphthyridine. A. Mangini and M. Colonna (*Gazzetta*, 1942, 72, 183—190, 190—197).—I. 2 : 6-Diaminopyridine (I) with  $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$  (II) at 140—180° gives 7-amino-2-hydroxy-4-phenyl-1 : 8-naphthyridine (III), m.p.  $< 345^\circ$  (hydrochloride, m.p.  $> 350^\circ$ ; picrate, decomp. 245—254°; *N*-Ac derivative, m.p.  $< 345^\circ$ ). At  $100^\circ$ , or in boiling  $\text{PhMe}$ , (I) and (II) give 2-amino-6-benzoylacetamidopyridine, m.p. 153—154°, which in conc.  $\text{H}_2\text{SO}_4$  gives (III), which can be characterised by diazotisation and decomp. to 2 : 7-dihydroxy-, m.p. 272—273°, chlorinated ( $\text{PCl}_5$ ) to 2 : 7-dichloro-4-phenyl-1 : 8-naphthyridine (IV), m.p. 158°. With  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ , (I) gives 7-amino-2-hydroxy-4-methyl-1 : 8-naphthyridine (Seide, A., 1927, 62) (*N*-Ac derivative, m.p.  $< 285^\circ$ ).

II. With  $\text{NaOMe}\cdot\text{MeOH}$  and  $\text{NaOEt}\cdot\text{EtOH}$ , (IV) gives 2 : 7-dimethoxy-, m.p. 156°, and 2 : 7-diethoxy-4-phenyl-1 : 8-naphthyridine, m.p. 87—88°. With boiling  $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , (IV) gives the 2 : 7-bis-*p*-phenetyl-amino-compound, m.p. 222—223° (decomp.), and with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ , followed by  $\text{HCl}$  the dihydrochloride, m.p. 253—254°, of



2 : 7-bishydrazino-4-phenyl-1 : 8-naphthyridine (bis-*p*-nitrobenzylidene derivative, m.p. 327—328°), which with  $\text{NaNO}_2\cdot\text{HCl}$  gives 1 : 2 : 7 : 8-ditriazolo-4-phenyl-1 : 2 : 7 : 8-tetrahydro-1 : 8-naphthyridine (V), darkens 200—202°, explodes  $203^\circ$ . 2 : 7-Dichloro-4-methyl-1 : 8-naphthyridine (VI) (Seide, *loc. cit.*) with  $\text{NaOMe}\cdot\text{MeOH}$  and  $\text{NaOEt}\cdot\text{EtOH}$  gives 2 : 7-dimethoxy-, m.p. 102—103°, and 2 : 7-diethoxy-4-methyl-1 : 8-naphthyridine, m.p. 72—73°. The electronic structure of (IV) and (VI) is discussed, and expressed in formula A. E. W. W.

**Triazines.**—See B., 1943, II, 7.

**Spectroscopic studies on porphyrins.**—See A., 1943, I, 80.

**Bile pigments.** XXXVI. Action of yeast and ascorbic acid on hæmins. E. Stier (*Z. physiol. Chem.*, 1942, 275, 155—165; cf. A., 1943, II, 46).—Acetylhaematoporphyrin  $\text{Me}_2$  ester Fe salt (I) or  $\text{Me}_4$  haematoporphyrin Fe salt in aerated 50% aq.  $\text{C}_5\text{H}_5\text{N}$  with yeast (*Saccharomyces cerevisiae*) at  $50^\circ$  for 30 min. yields the corresponding pyridineverdoparahæmatin (II), also obtained from (I) with pyrogallol- $\text{O}_2$  (cf. A., 1942, II, 382; Warburg *et al.*, A., 1930, 1199). (I) with ascorbic acid- $\text{O}_2$  at 55—60° gives (II) and, by

treatment with MeOH-HCl, acetylhaematoglucobilin Me<sub>2</sub> ester and a pigment with absorption max. (Et<sub>2</sub>O solution) at 532, 500, and <447 mμ. (Zn complex in Et<sub>2</sub>O, 630, 536, and <452 mμ.). Ascorbic acid-O<sub>2</sub> readily oxidises phyllohaemin ester to the corresponding pyridineverdoparahæmatin, which with MeOH-HCl affords phylloglaucobilin ester. Rhodohaemin Me<sub>2</sub> ester is similarly oxidised to rhodopyridineverdoparahæmatin Me<sub>2</sub> ester which, with MeOH-HCl, yields *rhodoglaucobilin Me<sub>2</sub> ester*, m.p. 226° (sinters at 210°), the first cryst. pigment of the bilitriene type; fluorescence spectra are compared with those of a typical bilidiene derivative. F. O. H.

**Chlorophyll. CXIV. Transition from the chlorophyll-*b* into the *a*-series.** H. Fischer and H. Gibian (*Annalen*, 1942, 552, 153—166).—Pyrophæophorbide *b* Me ester (I) is converted by NaOMe and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in C<sub>5</sub>H<sub>5</sub>N and MeOH containing NaOMe at 115—120° into some deoxophyllerythrin Me ester, m.p. 264°, and mainly inactive mesodeoxopyrophæophorbide *a* Me ester (II), m.p. 209—211°, thus establishing by direct experiment the intimate connexion of the chlorophyll-*a* and -*b* series. (I) is hydrogenated (Pd-100% HCO<sub>2</sub>H) to mesodeoxopyrophæophorbide *a* Me ester, dimorphous, m.p. ~186° or 204°, [α]<sub>D</sub><sup>20</sup> -645° ± 115° in COMe<sub>2</sub>, identical with that prepared from pyrophæophorbide *a* Me ester, thus establishing the identical steric arrangement of substituents in the two chlorophyll series. Mesopurpurin 3-Me ester, N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, NaOMe-MeOH, and C<sub>5</sub>H<sub>5</sub>N at 115—120° afford inactive mesophyllochlorin Me ester, m.p. 166—167°, with some phylloporphyrin, m.p. 234°. Pyrophæophorbide *a* is converted by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O at 100° in a sealed tube or in open vessels into optically inactive mesopyrophæophorbide *a* Me ester (III), m.p. 205—206° (Zn complex salt, m.p. 158°), also obtained similarly from pyrophæophorbide *b* Me ester. The prep. of (II) from (III) by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O or H<sub>2</sub>-Pd-100% HCO<sub>2</sub>H is described. The action of Pd and 100% HCO<sub>2</sub>H on phæophorbide *a* gives a small amount of (II), much decomposed material, and (?) deoxophæoporphyrin *a*<sub>5</sub> Me<sub>2</sub> ester, m.p. 287°, also obtained from phæophorbide *b*. Reduction of purpurin 7-Me<sub>2</sub> ester, 18-Me ester, and 18-Me ester imide leads to much decomposed material and the spectrum of the corresponding meso-compound. Sucrose and cholesterol are unchanged by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, NaOMe-MeOH, and C<sub>5</sub>H<sub>5</sub>N at 100°. H. W.

**Constitution of the prosthetic group of cytochrome-*c*.** K. Zeile and H. Meyer (*Z. physiol. Chem.*, 1940, 265, 22; cf. A., 1940, II, 110).—The porphyrin-*c* isolated by the authors was the prosthetic group of cytochrome-*c*, whilst Theorell's product (A., 1939, II, 394) resulted from recombination of products of hydrolysis. W. McC.

**Pyrazoleanthrone dyes.**—See B., 1943, II, 111.

**Nucleic acids. XXI. Tetranucleotide of yeast- and thymonucleic acid.** H. Brederick and E. Hoepfner [with I. Jochmann and A. Martini (*Ber.*, 1942, 75, [B], 1086—1095)].—Analyses of the deaminated tetranucleotide of thymonucleic acid agree with the formula C<sub>39</sub>H<sub>48</sub>O<sub>28</sub>N<sub>12</sub>P<sub>4</sub>. The mol. wt. of thymic acid determined by the diffusion method is 1067 (calc. 992). Yeast-nucleic acid, purified through the Pb salt, is converted by warming with 0.5% NaOH at 50° for 10 min. into the corresponding tetranucleotide (I). Titration shows the presence of a pentabasic acid and the increase in acidity after fission with alkali corresponds with 3 equivs. Analyses and determinations of mol. wt. support the formula C<sub>38</sub>H<sub>49</sub>O<sub>28</sub>N<sub>15</sub>P<sub>4</sub>, which is supported by the determination of guanine and adenine and analyses of the Mg salt. Deamination of (I) affords xanthine, hypoxanthine, and uracil. Methylation (Me<sub>2</sub>SO<sub>4</sub>) of (I) in feebly alkaline medium gives a product in which fission has not occurred and which is hydrolysed by HCl-MeOH to 1 : N<sup>2</sup>-dimethylguanine, 1 : N<sup>6</sup>-dimethyladenine, and 1 : N<sup>6</sup>-dimethylcytosine. (I) is therefore (OH)<sub>2</sub>PO·O·RB·[O·PO(OH)·O·RB]<sub>2</sub>·O·PO(OH)·O·RB (R = ribose; B = base). H. W.

**Fulminic synthesis of isooxazole derivatives. III.** A. Quilico and L. Panizzi (*Gazzetta*, 1942, 72, 155—165).—C<sub>2</sub>Na<sub>2</sub> in Et<sub>2</sub>O with moist CHI·N·OH (I) [prep. from Hg(CHI·N·OH)<sub>2</sub> and Na-Hg, followed by HI, described], followed by treatment with aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, gives the oxime (II), m.p. 147—148°, of isooxazole-5-aldehyde, an oil (p-nitrophenylhydrazone, m.p. 210—211°). Oxidation of (II) by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub> gives isooxazole-5-carboxylic acid. C<sub>2</sub>PhNa with (I) in Et<sub>2</sub>O, followed by aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, gives the oxime (III), m.p. 150—151°, of 5-phenylisooxazole-3-aldehyde, m.p. 61—62° (p-nitrophenylhydrazone, m.p. 225—228°), oxidised by CrO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-AcOH to 5-phenylisooxazole-3-carboxylic acid, also obtained from (III) and aq. KOH. With nitrous fumes, (III) in EtOH gives 3 : 4-(5' : 5''-diphenyl-3' : 3''-diisooxazolyl)-1 : 2 : 5-oxadiazole 2-oxide, m.p. 185—186°. Mechanisms of the two syntheses are discussed. E. W. W.

**Heterocyclic syntheses. II. Dichloromethylisooxazoles and corresponding aldehydes.** L. Panizzi (*Gazzetta*, 1942, 72, 99—108; cf. A., 1942, II, 394).—CHCl<sub>2</sub>·CO·CH<sub>2</sub>Ac with NH<sub>2</sub>OH·HCl in EtOH gives 5-methyl-3-dichloromethylisooxazole (I), b.p. 71—72°/5—6 mm., stable to conc. H<sub>2</sub>SO<sub>4</sub> and to dil. KOH or KOH-MeOH at the b.p., and dichloroacetonylacetoxime, CHCl<sub>2</sub>·CO·CH<sub>2</sub>·CMe<sub>2</sub>N·OH (II), m.p. 67.5—69.5, b.p. 136°/6 mm. (Ac derivative, oil). (II) resists benzoylation

and action of NH<sub>2</sub>OH or p-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>·NH·NH<sub>2</sub>; in boiling aq. HCl, (II) gives 3-methyl-5-dichloromethylisooxazole (III), m.p. 38—38.5°, b.p. 88—89°/11 mm. With NaOEt-EtOH at 170—180°, (II) and (III) give 5-methylisooxazole-3- and 3-methylisooxazole-5-aldehyde (cf. Quilico *et al.*, A., 1939, II, 523). CPhMe and CHCl<sub>2</sub>·CO<sub>2</sub>Et with NaOMe in Et<sub>2</sub>O give ω-dichlorobenzoylacetone, b.p. 170—171°/11 mm. [Cu salt, m.p. 196—197° (decomp.)], which with KOH gives CPhMe and CHCl<sub>2</sub>·CO<sub>2</sub>H, and with NH<sub>2</sub>OH·HCl in aq. EtOH gives dichloroacetonylbenzaldoxime (IV), m.p. 96—97° (Ac derivative, m.p. 82—83°). (IV) is unreactive like (II), but with conc. HCl gives 3-phenyl-5-dichloromethylisooxazole, m.p. 64.5—65°, which with NH<sub>2</sub>Ph at 120—130° gives 3-phenyl-5-bis-(p-aminophenyl)methylisooxazole, m.p. 167—168.5° [Ac<sub>2</sub> derivative, m.p. 156—157° (decomp.)], diazotisable. The possibility that (II) and (IV) have the isooxazoline structure,  $\text{N} \begin{array}{c} \text{R} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \end{array} \text{ (OH) } \cdot \text{CHCl}_2$ , is considered, but the true oxime structure is preferred. E. W. W.

**isooxazole-3 : 5-dicarboxylic acid.** C. Musante (*Gazzetta*, 1942, 72, 134—142).—CHPh·CH·CO·CH<sub>2</sub>·CO·CO<sub>2</sub>Et [Cu salt, m.p. 202—203° (decomp.)] and NH<sub>2</sub>OH·HCl in boiling EtOH give the Et ester (I), m.p. 113—113.5° (dibromide, m.p. 129°), of 5-styrylisooxazole-3-carboxylic acid [prep. from (I) and conc. HCl], m.p. 193—195° (decomp.) (Ag salt; Me ester, m.p. 145°), which at 200° gives, with ring-opening, α-cyano-α-benzylideneacetone, m.p. 98—99° [p-nitrophenylhydrazone (II), m.p. 207—208°], also obtained from CHPh·CH·CO<sub>2</sub>Et and MeCN (Na). On prolonged heating with alkali or acid, (II) gives 5-amino-1-p-nitrophenyl-3-styrylpyrazole, m.p. 172—173°. With boiling aq. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub>, (I) gives, with BzOH, isooxazole-3 : 5-dicarboxylic acid (+H<sub>2</sub>O, lost at 110°), m.p. 213° (decomp.) [Na<sub>2</sub> salt, darkens from 260°; Ag<sub>2</sub> salt, decomp. (semi-explosively) ~220°; Me<sub>2</sub> ester, m.p. 101°; diamide, darkens from 250°, no m.p. <300°; dianilide, m.p. 283° (variable) (decomp.)]. E. W. W.

**Thiazolines.**—See B., 1943, II, 7.

**Synthesis of possible lipophilic chemotherapeutics of the sulph-anilamide group.** S. Rajagopalan (*Current Sci.*, 1942, 11, 394—396).—Condensation (C<sub>5</sub>H<sub>5</sub>N) of the appropriate acid chlorides and sulphonamides yields the following N<sup>4</sup>-acylsulphonamides, having the m.p. given: cyclohexylsulphanilamide, 238°; n-butyryl-, 206°, n-hexoyl-, 197°, and n-heptyl-sulphapyridine, 193°; n-butyryl-, 244—246° (decomp.), n-hexoyl-, 198—199°, n-heptyl-, 202—203°, cyclohexoyl-, 222—223° (decomp.), palmityl-, 140—147°, and stearyl-sulphathiazole, 148—150°, and n-butyryl-, 224—225°, n-hexoyl-, 181—182°, n-heptyl-, 175—176°, and cyclohexoyl-sulphathiazoline, 220°. N<sup>4</sup>-n-Hexoylsulphanilamide with the acid chloride in C<sub>5</sub>H<sub>5</sub>N yields N<sup>4</sup>-n-hexoyl-N<sup>1</sup>-acetyl-, 166—169° (decomp.), -n-butyryl-, 164—168°, -n-heptyl-, 148—152°, -cyclohexoyl-, 185—187°, -palmityl-, 123—126°, and -stearyl-sulphanilamide, 127—130°. Sulphanilamide with the acid chloride (2 mols.) in C<sub>5</sub>H<sub>5</sub>N yields N<sup>4</sup>N<sup>1</sup>-di-n-hexoyl-, 164—172°, -di-n-butyryl-, 217—220°, and -di-n-heptyl-sulphanilamide, 131—134°. A. Li.

**Thiazole sulphanilamides.**—See B., 1943, III, 88.

**Preparation of standard samples of] methylene-blue.** H. O. Moraw (*J. Assoc. Off. Agric. Chem.*, 1942, 25, 798—799).—Analyses are given. A. A. E.

## VII.—ALKALOIDS.

**Alkaloids of various plant species within the genus *Nicotiana*.** A. A. Shmuk and A. Borozdina (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 32, 62—65).—A method for separating and identifying nicotine (I), nornicotine (II), and anabasine (III) is described. 42 species have been examined and divided into groups in which the main alkaloid is (a) (I), (b) (II), (c) a mixture of (I) and (II), (d) (III). F. R. S.

**Salts of cinchona alkaloids.**—See B., 1943, III, 21.

**Salamander alkaloids. II. Samandarone and samandaridine, minor alkaloids in poison of fire and alpine salamanders.** C. Schopf and K. Koch (*Annalen*, 1942, 552, 37—61; cf. A., 1935, 97).—The bulk of the samandarine (I) is removed from the total alkaloids as the sparingly sol. hydrochloride or, better, hydrobromide. The residual alkaloids deposit samandarone (+1H<sub>2</sub>O) (II), m.p. 189°, [α]<sub>D</sub><sup>21</sup> -115.7° in COMe<sub>2</sub> [hydrochloride, m.p. 355° (decomp.)], softens at 350°; double salt with HgCl<sub>2</sub>, m.p. 246° (decomp.); corresponding salt from (I), m.p. 209° (decomp.)], the isolation of which is completed by its conversion into N-benzoylsamandarone and its semicarbazone, m.p. 255—257° (decomp.), softens at 253°. Samandaronesemicarbazone, has m.p. 308° (decomp.) [hydrochloride, m.p. 350—355° (decomp.)], softens at 275°. (I) + (II) constitute 70—75% of the Et<sub>2</sub>O-sol. bases of the alpine salamander. The hydrochlorides remaining after removal of (I) contain samandaridine hydrochloride (+2H<sub>2</sub>O and anhyd.) (III), m.p. 343° (decomp.), sparingly sol. in H<sub>2</sub>O; the base appears to be present in the male but not in the female alpine salamander. In addition to (I) and (II) the fire salamander contains at least one primary or sec. base without ketonic character and a further ketonic primary or sec.

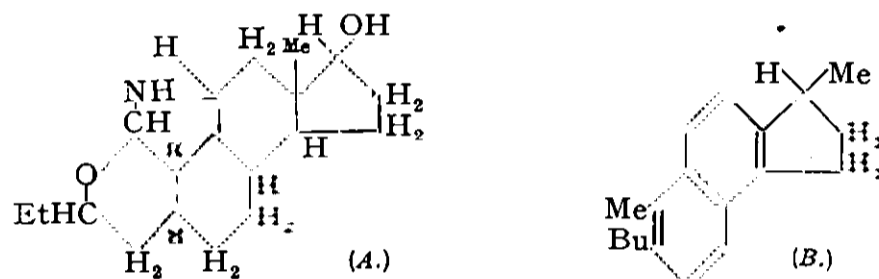
base; one or more *tert.* bases are also present. Treatment of (III) with  $\text{NH}_3$  affords *samandaridine* (IV),  $\text{C}_{21}\text{H}_{31}\text{O}_3\text{N}$ , m.p.  $289^\circ$ ,  $[\alpha]_D^{25} +29.5^\circ$  in 2N-AcOH [*hydrobromide*, m.p.  $346^\circ$  (decomp.); *hydriodide*, decomp.  $315^\circ$ ; *nitrate*, m.p.  $255^\circ$  (decomp.), softens at  $253^\circ$ ]. N in (IV) is *sec.* since (IV) is converted by MeI into *N-methylsamandaridine methiodide*, m.p.  $301^\circ$  (decomp.), by  $\text{HNO}_2$  into *N-nitrososamandaridine*, m.p.  $278^\circ$  (decomp.), which does not react with  $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ , and by  $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$  at room temp. into the non-basic *N-acetylsamandaridine*, m.p.  $228-229^\circ$ , softens at  $227^\circ$ . (IV) does not contain OH (Zerevitinov) and the presence of  $>\text{CO}$  could not be detected with  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$  or  $\text{NH}_2\cdot\text{OH}$ . (IV) is transformed by  $\text{KOH}-\text{EtOH}$  into *samandaridic acid*,  $\text{C}_{21}\text{H}_{33}\text{O}_4\text{N}$ , m.p.  $284-287^\circ$ , foams at  $279^\circ$  [*Ag salt* (+ $2\text{H}_2\text{O}$ ), decomp.  $205^\circ$ ]. (IV) therefore contains a lactone group but the nature of the third O could not be established. (IV) does not contain a double linking since it does not decolorise  $\text{KMnO}_4$  in hot  $\text{H}_2\text{SO}_4$ , is indifferent towards Br in AcOH, and does not absorb  $\text{H}_2$  catalytically. Like (I) it appears to be composed of three carbocyclic rings. When exposed to air in conc. HCl (II) and (IV) do not give the blue-violet colour characteristic of (I). H. W.

**Salamander alkaloids. III. Constitution of samandarine.** C. Schöpf and K. Koch [with W. Contzen] (*Annalen*, 1942, 552, 62—105; cf. A., 1935, 97).—Hydroxydihydrode-*N*-dimethylsamandarine (I), obtained by addition of  $\text{H}_2\text{O}$  to de-*N*-dimethylsamandarine (II), contains CO in addition to the new OH since it gives an *oxime*, m.p.  $204-206^\circ$  (slight decomp.; softens at  $203^\circ$ ), resinified by  $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$  and a *semicarbazone* (+1EtOH), m.p.  $168-169^\circ$  (decomp.). (I) does not appear to be affected by Na-EtOH,  $\text{Pb}(\text{OAc})_4$  in AcOH at  $60^\circ$ , or  $\text{HIO}_4$  in 2N-AcOH at  $65^\circ$ . Hydroxydihydrode-*N*-dimethylsamandarone (III), new m.p.  $154-155^\circ$  after softening at  $145^\circ$  (hydriodide, new m.p.  $272^\circ$ ), likewise gives an *oxime*. The conversion of the de-bases which contain a double linking and ethereal O into the hydroxydihydrode-bases which contain newly formed CO and OH but no double linking is explicable only on the assumption that they are enol ethers. (II) and (I) therefore contain the respective arrangements,  $>\text{C}\cdot\text{NMe}_2$ ,  $>\text{C}:\text{CH}\cdot\text{O}\cdot\text{CH}<$ ,  $>\text{CH}(\text{OH})$  and  $>\text{C}\cdot\text{NMe}_2$ ,  $>\text{CH}\cdot\text{CHO}$ ,  $\text{OH}\cdot\text{CH}<$ ,  $>\text{CH}(\text{OH})$ . The de-bases of samandarone (IV) and deoxysamandarine (V) contain  $>\text{C}\cdot\text{NMe}_2$ ,  $>\text{C}:\text{CH}\cdot\text{O}\cdot\text{CH}<$ ,  $>\text{CO}$  and  $>\text{C}\cdot\text{NMe}_2$ ,  $>\text{C}:\text{CH}\cdot\text{O}\cdot\text{CH}<$ ,  $>\text{CH}_2$ . For the corresponding hydroxydihydro-bases the corresponding formulæ are valid, viz.,  $>\text{C}\cdot\text{NMe}_2$ ,  $>\text{CH}\cdot\text{CHO}$ ,  $\text{OH}\cdot\text{CH}<$ ,  $>\text{CO}$  and  $>\text{C}\cdot\text{NMe}_2$ ,  $>\text{CH}\cdot\text{CO}$ ,  $\text{OH}\cdot\text{CH}<$ ,  $>\text{CH}_2$  or the forms  $>\text{C}\cdot\text{NMe}_2$ ,  $>\text{CH}\cdot\text{CH}(\text{OR})\cdot\text{O}\cdot\text{CH}<$ ,  $>\text{CO}$  and  $>\text{C}\cdot\text{NMe}_2$ ,  $>\text{CH}\cdot\text{CH}(\text{OR})\cdot\text{O}\cdot\text{CH}<$ ,  $>\text{CH}_2$ . The  $\text{H}_2$ -bases obtained by catalytic reduction of (I) and de-*N*-dimethylsamandarone correspond with  $>\text{C}\cdot\text{NMe}_2$ ,

$>\text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}<$ ,  $>\text{CH}\cdot\text{OH}$  and  $>\text{C}\cdot\text{NMe}_2$ ,  $>\text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}\cdot$ ,  $>\text{CO}$ . Samandarine (VI), (IV), and (V) contain the grouping  $>\text{C}\cdot\text{NH}\cdot\text{C}\cdot\text{CH}\cdot\text{O}\cdot\text{C}<$  since (III) under the influence of boiling  $\text{Ac}_2\text{O}$  suffers partial re-closure of the N ring and re-formation of the O bridge, giving a compound converted by KI into *N-methylsamandarone methiodide* (+ $1\text{H}_2\text{O}$ ), m.p.  $275-276^\circ$  (decomp.; softens at  $274^\circ$ ), and de-*N*-dimethylsamandarone, m.p.  $145^\circ$  (softens at  $143^\circ$ ), which is itself indifferent to boiling  $\text{Ac}_2\text{O}$ . (VI), (IV), and (V) therefore receive the partial structures  $>\text{C}\cdot\text{NH}\cdot\text{CH}(\text{CH}')\cdot\text{O}\cdot\text{CH}<$ ,  $>\text{CH}\cdot\text{OH}$ ,  $>\text{C}\cdot\text{NH}\cdot\text{CH}(\text{CH}')\cdot\text{O}\cdot\text{CH}\cdot\text{CO}$ , and  $>\text{C}\cdot\text{NH}\cdot\text{CH}(\text{CH}')\cdot\text{O}\cdot\text{CH}\cdot\text{CH}_2$ , respectively. This "aldehyde-ammonia" formula of (VI) explains the formation of methyl- (VII) and phenyl-samandiol (VIII) from (VI) and the requisite Grignard reagent since (VI) may be regarded as containing masked CO. (VII) and (VIII) contain therefore the arrangement,  $>\text{C}\cdot\text{NH}\cdot\text{CH}(\text{CH}')\cdot\text{R}$  in which R = Me or Ph. Further, the newly introduced OH is *sec.* since (VII) and (VIII) are oxidised to methyl- and phenyl-samandione. The non-reactivity of (II) and dihydrode-*N*-dimethylsamandarine is due to the absence of the sufficiently reactive "aldehyde-ammonia" group. The structure also explains the evolution of  $\text{N}_2$  in addition to that of N oxides observed when *N*-nitrososamandarine is boiled with 20% HCl, reaction being expressed:  $>\text{C}\cdot\text{N}(\text{NO})\cdot\text{CH}\cdot\text{O}\cdot\text{CH}< \rightarrow \text{OH}\cdot\text{CH}\cdot\text{O}\cdot\text{CH}< + [\text{C}\cdot\text{NH}\cdot\text{NO}] \rightarrow \text{C}\cdot\text{OH} + \text{N}_2$ . (VI) is very stable towards acid hydrolysis, its hydrochloride being unaffected by  $\text{H}_2\text{O}$  at  $140-150^\circ$  or at  $225^\circ$  for 13 hr. Boiling 10%  $\text{HClO}_4$  is without considerable action but at  $140-150^\circ$  a strongly unsaturated, amorphous base is obtained. Similarly boiling conc. HCl yields  $\text{CO}_2$  and amorphous products. Samandesone (IX), new m.p.  $194-195^\circ$ , gives a *methiodide*, m.p.  $304-305^\circ$  (softens after darkening, at  $289^\circ$ ), does not condense with  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  in boiling EtOH, and could not be degraded satisfactorily by  $\text{H}_2\text{O}_2$  in AcOH or alkaline solution. It is reduced by Na and EtOH to samandesol (X) in which the presence of a new OH is demonstrated by Zerevitinov's method and by the formation of an *acetate*, m.p.  $119-120^\circ$ . It gives a *hydriodide*, m.p.  $272-274^\circ$  (decomp.), and a *methiodide* (+ $1\text{H}_2\text{O}$ ), m.p.  $297^\circ$  (decomp.; softens at  $294^\circ$ ), and is oxidised by  $\text{CrO}_3$  in dil.  $\text{H}_2\text{SO}_4$  at  $100^\circ$  to (IX). Samandesonic acid (+ $1.5\text{H}_2\text{O}$ ) is obtained by the

action of  $\text{NH}_3$  on (IX). (X) similarly affords samandesolic acid, m.p.  $204-205^\circ$  (decomp.), which contains 3 active H (Zerevitinov). It is re-converted into (X) by sublimation in a high vac., by boiling 2N-HCl, by 6% HCl-MeOH at room temp., or by boiling abs. EtOH. (VI) is transformed by HBr-AcOH at  $65-75^\circ$  into *bromodeoxysamandarine*, m.p.  $159-160^\circ$ , converted by Zn dust and boiling AcOH into *deoxysamandarine*, m.p.  $123^\circ$  [*hydrochloride* (XI), m.p.  $305^\circ$  (decomp.) after softening], obtained also from *N*-benzoylsamandaronesemicarbazone and NaOEt in EtOH at  $180-190^\circ$ . (XI) is converted by aq.  $\text{Na}_2\text{CO}_3$  followed immediately by MeI into *N-methyldeoxysamandarine methiodide*, m.p.  $277-279^\circ$  (decomp.), converted by  $\text{Ag}_2\text{O}$  and subsequent heating at  $100-150^\circ/13$  mm. into *de-N-dimethyldeoxysamandarine*, m.p.  $78^\circ$ , softens at  $76^\circ$  [*hydriodide*, m.p.  $271-272^\circ$  (decomp.), softens at  $268^\circ$ ]. This with 3%  $\text{H}_2\text{SO}_4$  at  $100^\circ$  yields *hydroxydihydrode-N-methyldeoxysamandarine* (XII), m.p.  $122-123^\circ$ , softens at  $120^\circ$  (*hydriodide*, decomp.  $277^\circ$ ; softens at  $273^\circ$ ; *oxime*, m.p.  $168-169^\circ$ , softens at  $166^\circ$ ). (XII) is oxidised by  $\text{CrO}_3$  and dil.  $\text{H}_2\text{SO}_4$  at  $100^\circ$  to *deoxosamandesone*, m.p.  $99-100^\circ$ , softens at  $98^\circ$  [*hydriodide* (+ $1\text{H}_2\text{O}$  and anhyd.), m.p.  $258-259^\circ$  (decomp.), softens at  $256^\circ$ ]. *Deoxosamandesonic acid* [*hydrazide*, m.p.  $152^\circ$  (slight decomp.), softens at  $149^\circ$ ] has m.p.  $156-157^\circ$  (decomp.).

Dehydrogenation of (VI) by Se gives a hydrocarbon (XIII), b.p.  $85-95^\circ$  (bath)/0.003 mm., which could not be obtained cryst. and did not give a cryst. picrate. Cryst. products could not be obtained from it by nitration, bromination, or energetic oxidation with  $\text{KMnO}_4$  (towards which it is saturated at room temp.) or  $\text{HNO}_3$ . Its homogeneity is not established but, if assumed, analyses and



mol. wt. determinations indicate the formula  $\text{C}_{19}\text{H}_{24}$  as most probable and its formation therefore:  $\text{C}_{19}\text{H}_{31}\text{O}_2\text{N} \rightarrow \text{C}_{19}\text{H}_{24} + 2\text{H}_2\text{O} + \text{NH}_3$ . As it is not further changed when heated with much Se for 8 hr. at  $360-370^\circ$ , all 6-membered rings are already aromatic and (XIII) cannot be a phenanthrene hydrocarbon. Probably it is a  $\text{C}_{10}\text{H}_8$  derivative with a further carbocyclic ring. These observations and considerations of its origin and relationships suggest the constitutions A and B for (VI) and (XIII). H. W.

## VIII.—ORGANO-METALLIC COMPOUNDS.

**Preparation of a homologue of methylarsepedine, methyl-As-methylarsepedine.** E. V. Zappi and L. M. Simonin (*Ciencia*, 1942, 3, 160—161).—The Grignard compound from  $\text{Cl}\cdot[\text{CH}_2]_4\cdot\text{CHMeCl}$  and  $\text{AsMeCl}_2$  yields 1:2-dimethylarsepedine, b.p.  $169^\circ/760$  mm.,  $85^\circ/22$  mm. [*methiodide*, sublimes (sealed tube)  $340^\circ$ ; *methochloride*; *picrate*, m.p.  $231^\circ$  (decomp.)], which oxidises in air and with I in ligroin gives a resin. (Cf. A., 1916, i, 575.) F. R. G.

**Amylchlorophosphines.**—See B., 1943, I, 152.

**Mercuriphenyl salts.**—See B., 1943, II, 110.

**3-Bromosalicylic acid.** C. K. Kanvinde, A. N. Kothare, and V. V. Nadkarny (*Current Sci.*, 1942, 11, 397).— $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  and  $\text{Hg}(\text{NO}_3)_2$  at  $100^\circ$  give a Hg derivative which with Br in AcOH yields 2:3:1-OH $\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}_2\text{H}$  (60%). A. Li.

**Organo mercury compounds.**—See B., 1943, III, 89.

**Mercuration of pyridine.** C. K. Kanvinde, R. S. Borkar, A. N. Kothare, and V. V. Nadkarny (*J. Univ. Bombay*, 1942, 11, A, Part 3, 101—104).— $\text{C}_5\text{H}_5\text{N}$  when heated with  $\text{Hg}(\text{OAc})_2$  at  $178-180^\circ$  and treated with  $\text{H}_2\text{O}$  and NaCl yields 3-chloromercuripyridine (+ $\text{H}_2\text{O}$ ) (I), m.p.  $184^\circ$ , and a compound,  $\text{C}_5\text{H}_5\text{N}\cdot\text{Hg}_2\text{Cl}_2$ , decomp.  $203-205^\circ$ . 3-Bromo- (+ $\text{H}_2\text{O}$ ), m.p.  $148^\circ$ , and 3-iodo-mercuripyridine (+ $\text{H}_2\text{O}$ ), m.p.  $123^\circ$ , and the compounds,  $\text{C}_5\text{H}_5\text{N}\cdot\text{Hg}_2\text{Br}_2$ , decomp.  $223^\circ$ , and  $\text{C}_5\text{H}_5\text{N}\cdot\text{Hg}_2\text{I}_2$ , decomp.  $232-236^\circ$ , are similarly obtained, using KBr and KI. The filtrate from the pptn. of (I) with saturated aq. KI yields pyridine mercuri-tri-iodide,  $(\text{C}_5\text{H}_5\text{NH})\text{HgI}_3$ , m.p.  $152-153^\circ$ . A. Li.

**Effect of metallic chlorides on the reaction of Grignard reagents with phenyl styryl ketone and benzophenone.**—See A., 1943, II, 134.

## IX.—PROTEINS.

**Ferritin. II. apoFerritin of horse spleen.** S. Granick and L. Michaelis (*J. Biol. Chem.*, 1943, 147, 91—97).—A 3% solution of ferritin (I), which contains 20% of Fe, is dialysed with 2:2'-dipyridyl (II) through a Cellophane membrane against acetate buffer

at pH 4.6 through which  $N_2$  is passed and to which  $Na_2S_2O_4$  is added. The pink  $Fe^{II}$ -(II) complex diffuses through the membrane. Repetition of the procedure produces finally a colourless protein solution which crystallises on addition of  $CdSO_4$ . The cryst. form of the apoferritin (III) is identical with that of the Fe-containing (I). The mol. wt. is  $\sim 500,000$ . The only Fe compound which will re-combine with (III) to yield the brown (I) is the as yet uncharacterised colloidal compound present in the crystallisation liquors of (I). P. G. M.

## X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

**New stereoisomerides of methylbixin.** L. Zechmeister and R. B. Escue (*Science*, 1942, **96**, 229—230).—I catalysis, and melting of crystals, effects *cis-trans* conversion in methylbixin. The resulting mixture is separable into 8 stereoisomerides by chromatographic analysis using  $CaCO_3$  and  $C_6H_6$ -light petroleum mixtures. E. R. R.

**Catic acid.**—See B., 1943, II, 110.

**Tutin.** S. N. Slater (*J.C.S.*, 1943, 50—51).—An improved method of separation from the leaves and stem of *Coriaria lurida* gives tutin (I),  $C_{15}H_{18}O_8$ , m.p. 209—210° (*Ac* derivative, m.p. 177°), which is reduced ( $Pd-C-H_2$ ) to the  $H_2$ -derivative, m.p. 190—192° [*Br*-derivative, m.p. 257° (decomp.)]. Picotoxin (II) is similarly hydrogenated and brominated ( $Br-H_2O$ ) to *bromohydropicotoxinin*, m.p. 255° (decomp.). Bromination ( $Br-H_2O$ ) of (I) affords  $\alpha$ -, m.p. 256° (decomp.) (main product), and  $\beta$ -bromotutin, m.p. 237° (decomp.); similar bromination of (II) yields a mixture containing  $\beta$ -bromopicotoxinin, m.p. 282° (decomp.). It is considered that (I) is probably not identical with coriarine. F. R. S.

**Penicillin B, an antibacterial substance from *Penicillium notatum*.**—See A., 1943, III, 353.

## XI.—ANALYSIS.

**Apparatus for small-scale catalytic hydrogenation.**—See A., 1943, I, 103.

**Determination of methoxyl and ethoxyl groups.** L. M. Cooke and H. Hibbert (*Ind. Eng. Chem. [Anal.]* 1943, **15**, 24—25).—Total alkoxyl is determined by Vieböck's method. OMe is determined in the Vieböck apparatus by absorbing the MeI and EtI in  $EtOH-NMe_3$  followed by evaporation to dryness and  $NMe_3EtI$  separated by extraction with a saturated solution of  $NMe_4I$  in abs.  $EtOH$ . The residual  $NMe_4I$  is determined titrimetrically. J. D. R.

**Iodoform micro-test for the higher alcohols and ketones.** F. H. Stodola (*Ind. Eng. Chem. [Anal.]*, 1943, **15**, 72—73).— $CHI_3$  is prepared from the alcohol or ketone with  $KOH-I$  in  $MeOH$ , and recognised by the red colour formed on addition of  $m-C_6H_4(OH)_2$ . J. D. R.

**Determination of aliphatic nitrate esters. Colorimetric method.** H. Yagoda (*Ind. Eng. Chem. [Anal.]*, 1943, **15**, 27—29).—The blood, urine, or other sample is extracted with  $Et_2O$ , the extract washed and evaporated, and the residue dissolved in  $COMe_2$  and treated with a solution of *m*-xylenol in  $COMe_2$  and 62.5%  $H_2SO_4$ . The nitroxylenol formed is steam-distilled, the distillate treated with  $NaOH$ , and the yellow colour determined colorimetrically against similar preps. made with standard quantities of  $KNO_3$ . The method has been applied to nitroglycerin, erythritol tetranitrate, and pentaerythritol tetranitrate over the range 3.0—0.005 mg. J. D. R.

**Adsorption analysis of some triglycerides and fatty acids.**—See A., 1943, I, 124.

**Quantitative spectral analysis of molecules.** P. P. Schorigin (*J. Phys. Chem. Russ.*, 1941, **15**, 1072—1081).—Raman spectra can be used for quant. analysis of liquid mixtures, if the frequency of the exciting light, the width of the spectrograph slit, etc. are standardised. The frequency, intensity, and half-width of the Raman lines must be determined. A mixture of  $C_6H_6$ , PhMe, cyclohexane (I), methylcyclohexane (II), cyclopentane (III),  $CH_3Pr^iBu^v$ , and  $\Delta^a$ -heptene, and one containing  $C_6H_6$ , PhMe, (I), (II), (III), cyclohexene, and  $CCl_4$  have been analysed in this way; the largest relative error was 15% (*i.e.*, 11.5% instead of 10%). J. J. B.

**Iodometric micro-determination of pyruvic acid, glucose, and of a mixture of these two substances.** E. Haag and C. Dalphin (*Helv. Chim. Acta*, 1943, **26**, 246—250).—The iodometric determination of  $AcCO_2H$  ( $AcCO_2H = 6 I$ ) is only quant. if the amount of acid does not exceed 1.1 mg. Using Kolthoff's technique for glucose (I) this requires that at least 17.5 c.c. of 0.01N- $Na_2S_2O_3$  should be required for titrating the excess of I. Prolongation of the time of oxidation

from 10 to 50 min. does not affect the iodometric determination of (I). The application of the method to the simultaneous determination of (I) and  $AcCO_2H$  is described. H. W.

**Adsorption analysis: experimental arrangement and results with mixtures of glucose and lactose.**—See A., 1943, I, 139.

**Determination of free and acetylated sulphanilamide.** S. Anderson (*Ind. Eng. Chem. [Anal.]*, 1943, **15**, 29—30).—Sulphanilamide (I) and acetylsulphanilamide (II) are determined together in aq. solution by use of a Cenco replica grating spectrograph, using a  $H_2$  arc as the source of ultra-violet light. (I) absorbs all light below 310  $m\mu$ , and (II) absorbs only light below 286  $m\mu$ . By use of a fluorescent screen, the unknown solution is balanced against a known solution of (I), using filters absorbing below 310  $m\mu$  and also below 286  $m\mu$ . The former reading gives free (I), the latter total of free (I) and (II). Modifications are described which make the method applicable to blood. J. D. R.

**Acriflavine as internal indicator for sulphanilamide-nitrite titrations.** H. F. Frost (*Analyst*, 1943, **68**, 51).—Acriflavine gives a colour change from yellow to violet at the end-point in the diazotisation method (A., 1942, II, 388). S. B.

**[Determination of] halogens in halogenated fluoresceins.** J. H. Jones (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 944—947).—Determinations of Cl and Br by the Vieböck and Zacherl-Krainick methods in 100—200-mg. samples gave results  $\sim 98 \pm 1\%$  of calc. vals. A. A. E.

**Determination of 2-methyl-1:4-naphthaquinone and its solution in water.** F. Giral and S. Garcia Iglesias (*Ciencia*, 1942, **3**, 157—159).—The method of Novelli (A., 1941, II, 298) permits the determination of 2-methyl-1:4-naphthaquinone (I) to within 4—5  $\mu g$ . A solution prepared by adding 100 mg. of (I) in 1 c.c. of  $EtOH$  to 100 c.c. of 1% Na deoxycholate in  $H_2O$  at pH 7.0 is stable for 3—4 days. F. R. G.

**Determination of furfuraldehyde.** I. J. Duncan (*Ind. Eng. Chem. [Anal.]*, 1943, **15**, 162—164).—The plant material is distilled with 18.5—24%  $HCl$ , and the furfuraldehyde determined in the distillate by the  $NH_2Ph-AcOH$  colorimetric method, which is more accurate and sp. than the titration method. J. D. R.

**Fluorescence test for  $\beta$ -indolylacetic acid.** J. H. Hamence (*Analyst*, 1943, **68**, 13—14).—When heated with conc.  $H_2SO_4$  at 100° indolyl-3-acetic acid (I) gives a yellowish-green, indolyl-3-propionic acid gives a bluish, and indole gives a slight fluorescence. 0.02 mg. of (I) may be detected. S. B.

**Determination of nicotinic acid and sodium nicotinate.** L. E. Harris and B. I. Duis (*J. Amer. Pharm. Assoc.*, 1943, **32**, 31—32).—Determination of nicotinic acid (I) and Na nicotinate by pptn. as Cu nicotinate gives good results with solutions or tablets. The  $CuSO_4$  reagent does not form a ppt. with aneurin, riboflavin, or Ca pantothenate, but certain combinations and concns. of these substances cause low results in the assay of (I), whilst presence of rice bran, liver, or beef extracts causes high results. The method is not entirely satisfactory for determination of nicotinamide after hydrolysis to (I), unless hydrolysis is very carefully carried out with  $HNO_3$  and all  $NH_3$  subsequently removed. J. N. A.

**[Determination of] 8-hydroxyquinoline sulphate.** A. M. Allison (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 796—798).—Duggan's gravimetric procedure using phosphotungstic acid is subject to error arising from the solubility of the ppt. but could probably be improved. A. A. E.

**[Determination of] barbituric acid derivatives.** L. E. Warren (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 799—808).—Extraction with  $CHCl_3 + Et_2O$  gave satisfactory collaborative results. Precise procedure is recorded. A. A. E.

**Photochemical spectrum of cytochrome oxidase.**—See A., 1943, III, 272.

**[Determination of] quinine ethylcarbonate.** H. G. Underwood (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 824—828).—Acidimetric determination as quinine after extraction gives satisfactory results. A. A. E.

**Iodometric semimicro-determination of arsenic in sodium cacodylate and cacodylic acid.** V. Levine and W. M. McNabb (*Ind. Eng. Chem. [Anal.]*, 1943, **15**, 76—77).—The sample is digested with  $KHSO_4-H_2SO_4$ , and the resulting solution reduced with  $NaH_2PO_2$  followed by determination of As with I. J. D. R.

**Separation and determination of protein-sulphur, sulphide-sulphur, and other sulphur in sodium sulphide dispersions of keratin.** E. F. Potter and C. B. Jones (*Ind. Eng. Chem. [Anal.]*, 1943, **15**, 15—17).—The dispersion is heated with basic Al acetate, the  $H_2S$  evolved collected in  $Pb(OAc)_2$ , and the S determined, giving sulphide-S. The residual protein is collected and ignited with  $Mg(NO_3)_2$  and the protein-S determined as  $BaSO_4$ , and the residual S in the filtrate from the protein is oxidised with  $NaOBr$  and determined as  $BaSO_4$ . J. D. R.

## A., II.—Organic Chemistry

JUNE, 1943.

## I.—ALIPHATIC.

**Photochemical reactions of the halogens with aliphatic compounds.**—See A., 1943, I, 159.

**Production of isooctane.**—See B., 1943, II, 70.

**Progress of butadiene production.**—See B., 1943, II, 69.

**Kinetics and energetics of the high-temperature cracking of methane to acetylene.**—See A., 1943, I, 156.

**Polymerisation of acetylene to benzene.** P. Pascal and C. Coupard (*Compt. rend.*, 1942, 214, 757—759).— $C_2H_2$  passed over  $C-Al_4C_3$  at 700—725° yields  $C_6H_6$  (50—60), PhMe, PhEt, xylene, and  $CHPh\cdot CH_2$  (together 10—15),  $C_{10}H_8$  (10—15),  $Ph_2$  (5—10), and anthracene hydrocarbons (5—10%). A. Li.

**Alkyl halides containing a quaternary carbon atom.**—See B., 1943, II, 70.

**Action of halogen acids on alcohols in presence of benzene.** S. P. Walvekar, N. L. Phalnikar, and B. V. Bhide (*J. Indian Chem. Soc.*, 1942, 19, 409—413).—In the absence of  $C_6H_6$  the rate of action with HCl of EtOH,  $Pr^aOH$ ,  $Bu^aOH$ , and  $CH_2Bu^b\cdot OH$  follows the sequence  $Et > Pr^a > Bu^a > CH_2Bu^b$ . The rate, however, increases when  $C_6H_6$  is present and this increase is explained by solubility considerations. H. W.

**Aliphatic trisulphonylmethanes.** E. Samén (*Arkiv Kemi, Min., Geol.*, 1942, 15, B, No. 15, 8 pp.).— $Pr^aSH$  and boiling  $HCO_2H$  give  $CH(SPr^a)_3$ , b.p. 150—151°/9 mm., oxidised ( $Et_2O$ - $o$ - $CO_2H\cdot C_6H_4\cdot CO_2H$  at -10°) to *tri-n-propanesulphonyl-methane*, m.p. 235—237°, converted (halogen in  $H_2O$  or dil. NaOH) into the *-methyl bromide*, m.p. 142—143°, and *chloride*, m.p. 123—124°. Similarly prepared are  $CH(SO_2Bu^a)_3$ , m.p. 228—230°, *tri-n-butanessulphonylmethyl bromide*, m.p. 83—84°, and *chloride*, m.p. 57—58°.  $SO_2Et\cdot CH(SO_2Me)_2$ , m.p. 276—278°, affords *bismethanesulphonylethanesulphonylmethyl bromide*, m.p. 136—137°, and *chloride*, m.p. 149—150°. M.p. are corr.  $CH(SO_2Alk)_3$  are strong acids; conductivity data are given. A. T. P.

**Kinetics of the reaction between  $\gamma$ -ethylsulphonylbutan- $\beta$ -one and bromine in aqueous hydrobromic acid.**—See A., 1943, I, 156.

**Photochemical chlorination and sulpho-chlorination of paraffin hydrocarbons in carbon tetrachloride solution.**—See A., 1943, I, 159.

**Peroxides in isopropanol.** C. E. Redemann (*J. Amer. Chem. Soc.*, 1942, 64, 3049—3050).— $Pr^bOH$  rapidly forms peroxides in air in bright light, up to 0.36 mol. per l. being found in an old sample. R. S. C.

**Batyl alcohol.** N. Kornblum and H. N. Holmes (*J. Amer. Chem. Soc.*, 1942, 64, 3045—3046).— $CH_2\cdot CH\cdot CH_2\cdot ONa$  (I) and  $n-C_{18}H_{37}I$  at 60—65° give 70—79% of  $n-C_{18}H_{37}\cdot O\cdot CH_2\cdot CH\cdot CH_2$ , m.p. 28.5—29°, b.p. 150—152°/2 mm. (cf. Davies *et al.*, A., 1931, 62), converted by 30%  $H_2O_2$  in AcOH at 80—85° into batyl alcohol (55—67%), sinters 69°, m.p. 70—71° (corr.).  $CH_2\cdot CH\cdot CH_2\cdot OH$  and (I) at the b.p. condense to give high-boiling, unsaturated neutral and acidic products. R. S. C.

**Further attempted purification of vitamin- $A_2$ .** P. Karrer and E. Bretscher (*Helv. Chim. Acta*, 1942, 25, 1650—1653; cf. A., 1942, II, 185).—In pike-liver oil of the winter of 1941 the ratio vitamin- $A_2$ : $-A$  is greatly displaced in favour of  $-A_2$  in comparison with the summer oils of 1941 and 1942. After threefold chromatography over  $Ca(OH)_2$  followed by mol. distillation a product is obtained in which the  $-A$  band at 620 m $\mu$ . cannot be detected with certainty. It appears that the ratio of the max. extinction coeff. of the blue spectrum of the  $SbCl_3$  reaction and the ultra-violet spectrum differs in the cases of  $-A_2$  and  $-A$ . Degradation of the purest products with  $O_3$  gives a substance which yields  $CHI_3$  but is not identified with certainty as  $COMe_2$ . H. W.

**Preparation of pentaerythritol.**—See B., 1943, II, 71.

**Diacetone- $[diisopropylidene]$ -xylitol.** R. S. Tipson and L. H. Cretcher (*J. Org. Chem.*, 1943, 8, 95—98).—Xylitol is converted by  $COMe_2$  containing anhyd.  $CuSO_4$  and a little conc.  $H_2SO_4$  into *diisopropylidenexylitol*, m.p. 34—34.5°,  $[\alpha]_D^{25} \pm 0^\circ$  in  $COMe_2$ , transformed by  $p-C_6H_4Me\cdot SO_2Cl$  in dry  $C_5H_5N$  into the *p-toluenesulphonate*, m.p. 70—71°,  $[\alpha]_D^{25} \pm 0^\circ$  in abs. EtOH. When treated with NaI

in  $COMe_2$  at 100° this affords  $p-C_6H_4Me\cdot SO_3Na$  (I) in 94% yield. This reaction in the sugar series is characteristic of  $p-C_6H_4Me\cdot SO_2$  attached to a primary alcoholic group (cf. Oldham *et al.*, A., 1932, 254). Erythritol is converted by  $p-C_6H_4Me\cdot SO_2Cl$  in  $C_5H_5N$  into the *tetra-p-toluenesulphonate*, m.p. 165—166°, which with NaI in  $COMe_2$  gives (I) in 91% yield with apparently  $(CH_2\cdot CH)_2$ . Oldham's rule does not therefore apply to the sugar alcohols. H. W.

**$\beta\gamma\delta\epsilon$ - and a second dimethylene-D-mannitol.** W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, 65, 67—70).—D-Mannitol, 37%  $CH_2O$ , and conc. HCl at 100° give trimethylene-, m.p. 232° (cf. Schulz *et al.*, A., 1894, i, 438; 1896, i, 115; named mannitol triformacetal), and  $\alpha\gamma\delta\epsilon$ - or  $\alpha\gamma\epsilon\zeta$ -dimethylene-D-mannitol (I), m.p. 204—208°,  $[\alpha] -91.0^\circ$  in  $H_2O$ . D-Mannitol  $\alpha\zeta$ -dibenzoate with 37%  $CH_2O$  and dry HCl in dioxan at 0—5° gives  $\beta\gamma\delta\epsilon$ -dimethylene-D-mannitol  $\alpha\zeta$ -dibenzoate, m.p. 120—122°,  $[\alpha] +47.5^\circ$  in  $CHCl_3$ , converted by NaOMe-MeOH in  $CHCl_3$  at 5° into  $\beta\gamma\delta\epsilon$ -dimethylene-D-mannitol (II) (85%), m.p. 139°,  $[\alpha] +71.7^\circ$  in  $H_2O$  ( $\alpha\zeta$ -diacetate, m.p. 105—106°,  $[\alpha] +98.3^\circ$  in  $CHCl_3$ ). (II) gives a  $\alpha\zeta$ -di-p-toluenesulphonate, m.p. 164—165°,  $[\alpha] +68.1^\circ$  in  $CHCl_3$ , converted by NaI in  $COMe_2$  at 100° into the  $\alpha\zeta$ -diiodide (III) (98%), m.p. 196—197°,  $[\alpha] +49.7^\circ$  in  $CHCl_3$  (Micheel, A., 1932, 834). With Raney Ni- $H_2$ -NaOH in MeOH, (III) gives  $\beta\gamma\delta\epsilon$ -dimethylene- $\alpha\zeta$ -dideoxy-D-mannitol, m.p. 59—60°,  $[\alpha] +54.9^\circ$  in  $CHCl_3$  (cf. *loc. cit.*), and thence (boiling 10% HCl)  $\alpha\zeta$ -dideoxy-D-mannitol, m.p. 147—148°,  $[\alpha] -22.5^\circ$  in  $H_2O$ , which with  $HIO_4$  gives 1.90 MeCHO, proving the  $\alpha\zeta$ -position of the deoxy-groups. (II) does not reduce  $HIO_4$ , gives a *diacetate*, m.p. 166°,  $[\alpha] -64.4^\circ$  in  $CHCl_3$ , *dibenzoate*, m.p. 180°,  $[\alpha] +9.5^\circ$  in  $CHCl_3$ , and *di-p-toluenesulphonate*, m.p. 147°,  $[\alpha] -37.3^\circ$  in  $CHCl_3$  (unaffected by NaI in  $COMe_2$  at 100° or in  $Ac_2O$  at 140°). M.p. are corr.  $[\alpha]$  are  $[\alpha]_D^{20}$ . R. S. C.

**Ring structure of polygalitol.** N. K. Richtmyer and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, 65, 64—67).—Polygalitol (I) (prep. from roots of *Polygala senega*, N.F.; sucrose also present), m.p. 141—142°,  $[\alpha]_D^{20} +42.5^\circ$  in  $H_2O$  (tetra-acetate, dimorphic, m.p. 65—67° and 73—74°), is crystallographically identical with aceritol. (I) and styracitol (II) consume 2 equivs. of  $NaH_5I_2O_6$ , giving 1  $HCO_2H$ , and consume 2  $HIO_4$ , giving a dialdehyde, converted by  $Br-Sr(OH)_2$  into *Sr D-hydroxymethyldiglycollate*,  $+4H_2O$ ,  $[\alpha]_D^{20} -13.9 \pm 0.4^\circ$  (anhyd.) in  $H_2O$ ,  $+45.4-45.6 \pm 0.4^\circ$  (calc. for acid) in  $N-HCl$ . (I) and (II) are isomeric  $\alpha\epsilon$ -anhydro-D-hexitols. R. S. C.

**$\beta$ -Sulphinopropionic acid and related compounds.** J. A. Reuterskiöld (*Arkiv Kemi, Min., Geol.*, 1941, 14, B, No. 16, 6 pp.).— $Cl\cdot[CH_2]_2\cdot CO_2H$  and  $(CH_2\cdot SH)_2$  in slightly alkaline solution at 0° give *ethane- $\alpha\beta$ -di(thiol- $\beta'$ -propionic acid)*,  $(CO_2H\cdot[CH_2]_2\cdot S\cdot CH_2)_2$ , m.p. 158.5—159.5°. Oxidation with 5% aq.  $KMnO_4$  gives the corresponding *disulphone*, m.p. 300° (decomp.), converted by aq. NaOH (1 day), followed by  $SrCl_2\cdot 6H_2O$  (neutralise with 0.5N-HCl), into the *Sr salt* ( $+3H_2O$ ), and thence into the *Ag<sub>2</sub> salt*, and finally  *$\beta$ -sulphinopropionic acid*, m.p. 73—76°, resolidifies at  $\sim 100^\circ$  and re-melts at 122—124°. A. T. P.

**Reactions of atoms and free radicals in solution. IV. Decomposition of acetyl peroxide in aliphatic acids. Synthesis of succinic acid and its substitution derivatives.** M. S. Kharasch and M. T. Gladstone (*J. Amer. Chem. Soc.*, 1943, 65, 15—17; cf. A., 1942, II, 393).— $Ac_2O_2$  (0.144) in AcOH at 85—95° gives  $CO_2$  (0.22),  $CH_4$  (0.212),  $MeOAc$  (0.0072), and  $(CH_2\cdot CO_2H)_2$  (0.072 mol.), in  $Pr^bCO_2H$  0.066 mol. gives  $CO_2$  (0.088),  $CH_4$  (0.08),  $MeOAc$  (0.0072), and  $(CMe_2\cdot CO_2H)_2$  (0.028 mol.), m.p. 191—192° (anil, m.p. 85°), and in  $CH_2Cl\cdot CO_2H$  gives  $CO_2$ ,  $CH_4$ , and *meso*-( $CHCl\cdot CO_2H$ )<sub>2</sub>. Reaction is postulated as  $Ac_2O_2 \rightarrow Me\cdot + AcO\cdot + CO_2$ ,  $AcOH + Me\cdot \rightarrow CH_4 + \cdot CH_2\cdot CO_2H \rightarrow (CH_2\cdot CO_2H)_2$  etc., also  $AcO\cdot \rightarrow MeOAc + CO_2$ .  $Ac_2O_2$  in  $AcCl$  gives  $COCl\cdot[CH_2]_2\cdot CO_2Ac$  (no details). R. S. C.

**Fats. CIII. Reaction of tetranitromethane with fatty acids and fats.** H. P. Kaufmann [with P. Kirsch, B. W. King, and L. S. Huang] (*Ber.*, 1942, 75, [B], 1201—1214).—Fatty acids with a triple linking, like other compounds of the  $C_2H_2$  series, do not give a colour with  $C(NO_2)_4$ . Fatty acids and fats with isolated double linkings give colours which darken as the I val. increases. Glycerides and fatty acids with conjugated unsaturated linkings give in 10% solution a blood-red colour which weakens and tends towards

orange with increasing dilution. With trebly conjugated-unsaturated compounds the colour persists but fades to rose. The limit of detection of elæostearic acid in  $\text{CCl}_4$  is 0.03% whilst recognisable reaction is observed with tung oil (1 in 1000). All conjugated-unsaturated systems do not give a colour with  $\text{C}(\text{NO}_2)_4$ . Great differences are observed between the behaviour of *cis-trans* isomeric fatty acids. For the development of full colour a very large excess of  $\text{C}(\text{NO}_2)_4$  is required. The Lambert-Beer law is obeyed. The relationship between I val. and extinction val. for solutions of oleic acid in  $\text{CHCl}_3$  is approx. rectilinear but its use for the photometric determination of the I val. of unknown fats is not considered sufficiently accurate. The possibility that the action of  $\text{C}(\text{NO}_2)_4$  on fatty acids may cause elaidinisation is established by the observed conversion of oleic (I) into elaidic (II) and of erucic into brassidic acid. Olive oil yields palmitodielaidin. Polymerisation phenomena are observed with linoleic and linolenic acid, chaulmoogra and cod-liver oil but it is undecided whether the action is a true polymerisation or a ring formation with co-operation of O (dioxan system). (II) is oxidised by  $\text{C}(\text{NO}_2)_4$  in boiling  $\text{CCl}_4$  to nonaldehyde (III) and nonoic (IV),  $\theta$ -diketostearic, and azelaic acid with unidentified polymerised material. Under similar conditions stilbene affords benzil,  $\text{BzOH}$ , and  $\text{PhCHO}$  and  $(\text{CHMe})_2$  yields  $\text{AcOH}$ ,  $\text{MeCHO}$ , and  $\text{Ac}_2$ . (I) gives the same products as (II) possibly by reason of preliminary elaidinisation. Erucic acid is converted into (III), (IV), brassylic acid (Me ester, m.p. 35–36°), and  $\mu\nu$ -diketobehenic acid, m.p. 91–92°. Attempts to isolate the primary adducts on which the colour changes depend were unsuccessful. The reaction products include  $\text{CH}(\text{NO}_2)_3$ ,  $\text{NO}$ , and  $\text{CO}_2$ . Not infrequently the reaction leads to explosions for no obvious reason. H. W.

**Fatty acids. XI. Isolation of linoleic acid from vegetable oils by low-temperature crystallisation.** J. S. Frankel, W. Stoneburner, and J. B. Brown (*J. Amer. Chem. Soc.*, 1943, 65, 259–262).—Sesamé, cotton-seed, grape-seed, and poppy-seed oil yield, by crystallisation from  $\text{COMe}_2$  (cf. A., 1941, II, 239), 97–100% pure  $\alpha$ -linoleic acid, but olive oil gives mixed stereoisomerides R. S. C.

**Course of autoxidation reactions in polyisoprenes and allied compounds. IV. Isolation and constitution of photochemically formed methyl oleate peroxide. V. Observations on fish-oil acids.** E. H. Farmer and D. A. Sutton. **VI. Peroxidation of rubber.** E. H. Farmer and A. Sundralingam (*J.C.S.*, 1943, 119–122, 122–125, 125–133).—IV. Mol. distillation or chromatographic analysis of the product of autoxidation at 35° of Me oleate yields an unsaturated *mono*- (with a small amount of di-)hydroperoxide, reduced ( $\text{H}_2$ ,  $\text{PtO}_2$  in  $\text{EtOH}$ ) to Me hydroxystearate or (Al-Hg in  $\text{Et}_2\text{O}$ ) to Me hydroxylolate;  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  effects partial reduction.

V. Me dodecahexaenoate rapidly absorbs  $\text{O}_2$ , giving peroxides which decompose spontaneously into oxygeno-compounds (some of which contain only 1 atom of absorbed O per  $\text{C}_{23}$  chain) and scission products (responsible for the fishy odour). These products and those from ling oil show increased light absorption.

VI. Peroxide formation is 80–90% in the early stages of oxidation ( $\text{O}_2$ ) of rubber at 35° in  $\text{C}_6\text{H}_6$ , but steadily decreases as oxidation proceeds. Determinations of I val. and active H val. show that  $\text{O}_2$  initially enters active  $\text{CH}_2$  groups as  $\text{O}_2\text{H}$  groups, secondary reactions giving OH-compounds. Oxidative scission occurs from the outset, the final products being neutral, mol. wt. a few thousand, and acidic substances, mol. wt. 700–800, the quantity of  $\text{O}_2$  absorbed being > adequate to account for the scissions. Small quantities of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are formed at all stages, elimination of  $\text{H}_2\text{O}$  continuing after the oxidation products have been isolated. A. Li.

**High polymerides and new rules.** S. Weiner (*J. Chem. Educ.*, 1942, 19, 514–516). L. S. T.

**Configurative relationship between optically active lactic and thiolactic acids.**—See A., 1943, I, 154.

**Synthesis of the *cis*- and *trans*-form of an isoambrettolide and of civetone.** H. Hunsdiecker (*Naturwiss.*, 1942, 30, 587).—Aleuritic acid (A., 1927, 447) when heated with  $\text{AcOH-HBr}$  affords  $\theta$ -tri-bromopalmitic acid, which with  $\text{Zn-EtOH}$  gives  $\alpha$ -bromo- $\Delta^6$ -hexadecenoic acid in the olein and elaidin (I), m.p. 42°, forms. On heating with  $\text{K}_2\text{CO}_3$  in  $\text{COMeEt}$  these yield the corresponding hexadecenolides differing from ambrettolide only in the position of the double linking. The elaidin form (II) of isoambrettolide is a viscous fluid, b.p. 131°/0.7 mm., yielding with  $\text{H}_2$   $\alpha$ -hexadecanolide. On hydrolysis (II) affords a  $\alpha$ -hydroxy- $\Delta^6$ -hexadecenoic acid, m.p. 70°. The olein form was not obtained pure. The synthesis of natural civetone was similar. (I) was converted via the acid chloride into Me  $\rho$ -bromo- $\beta$ -keto- $\Delta^6$ -hexadecenoate, m.p. 25°. The corresponding I-compound, m.p. 35°, on intramol. acetoacetic ester condensation gives Me civetone- $\alpha$ -carboxylate, b.p. 175°/0.2 mm., which on hydrolysis and elimination of  $\text{CO}_2$  yields natural civetone, which is thus the elaidin form. J. H. B.

**Isolation and constitution of an acid from the root bark of *Ixora coccinea* (Linn.).** A. R. S. Kartha and K. N. Menon (*Proc. Indian Acad. Sci.*, 1943, 17, A, 11–15).—The light petroleum extract of the fresh root bark consists of a liquid,  $\Delta^6$ -heptadecadienoic acid

(Me ester, b.p. 195–196°/5 mm.; Et ester, b.p. 215–216°/5 mm.), which may be that obtained by Chonowsky (A., 1909, i, 760). The residue from the bark extracted with  $\text{EtOH}$  yielded mannitol.

F. R. G.

**Structure of arachidonic and linoleic acids.** C. L. Arcus and I. Smedley-Maclean (*Biochem. J.*, 1943, 37, 1–6).—Ozonolysis and oxidation of methyl arachidonate with  $\text{KMnO}_4$  in  $\text{COMe}_2$  confirm that arachidonic acid is  $\Delta^{8,11}$ -eicosatetraenoic acid (cf. Dolby *et al.*, A., 1941, II, 4). Contrary to the results of Takahashi, ozonolysis of Et linoleate shows that the acid is  $\Delta^{9,12}$ -octadecadienoic acid.

J. N. A.

**Maleic anhydride as reagent for conjugated diolefines.** R. F. Robey (*Science*, 1942, 96, 470).—Certain dienes fail to respond to this reagent. E. R. R.

**Determination of 2:3-diketo-*l*-gulonic acid.**—See A., 1943, III, 448.

**Molecular compound of optically active di-( $\alpha$ -carboxyethyl) disulphide and  $\alpha\alpha'$ -dithioladipic acid.**—See A., 1943, I, 153.

**Production of aldehydes and ketones from nitro-paraffins.** K. Johnson [with E. F. Degering] (*J. Org. Chem.*, 1943, 8, 10–11).—The  $\text{NO}_2$ -paraffin is dissolved in dil. aq.  $\text{NaOH}$  and the solution is added dropwise to ice-cold, dil.  $\text{H}_2\text{SO}_4$  with good stirring.  $\text{N}_2\text{O}$  is immediately evolved.  $\text{Ca}(\text{OH})_2$  may replace  $\text{NaOH}$  but more time must be given for the initial reaction. The prep. of  $\text{COMe}$ ,  $\text{MeCHO}$ ,  $\text{EtCHO}$ ,  $\text{Pr}^\alpha\text{CHO}$ ,  $\text{Pr}^\beta\text{CHO}$ , and  $\text{COMeEt}$  is described. The reaction is generally applicable for the synthesis of aldehydes and ketones. H. W.

**Structural effects of unsaturation and hyperconjugation in aldehydes, nitriles, and chlorides.**—See A., 1943, I, 144.

**Catalytic reduction by formic acid under pressure. I. Preparation of aldehydes from carboxylic acids with titanium dioxide as catalyst.** R. R. Davies and H. H. Hodgson (*J.C.S.*, 1943, 84–86).—Nonoic, undecenoic, lauric, benzoic, salicylic, and *p*-chloro- and *p*-sulphobenzoic acids are reduced by  $\text{HCO}_2\text{H}$  at 250–260 ( $\text{TiO}_2$ ) in a special apparatus to the aldehydes (22, 25, 31, 37, 92, 41, and 22% yield respectively). Butyric and heptonic acids do not react, and *p*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$  gives chiefly  $\text{PhNO}_2$ . A reaction mechanism is suggested. A. Li.

**Electrolytic oxidation. XIII. Formaldehyde.**—See A., 1943, I, 159.

**Hydrogenation of formaldehyde.**—See B., 1943, II, 71.

**Ketone alcohols. I. Derivatives of  $\beta$ -methylpentan- $\beta$ -ol- $\delta$ -one.** C. E. Miller. **II. Derivatives of polymerisation of pentan- $\gamma$ -one.** K. C. Odney and C. E. Miller (*J. Amer. Pharm. Assoc.*, 1942, 31, 516–518, 518–519).—I.  $\text{OH-CMe}_2\text{-CH}_2\text{-COMe}$  (I) (1 mol.) shaken with  $\text{HCl}$  ( $d$  1.175; 3 mols.) at room temp. gives  $\text{CMe}_2\text{Cl-CH}_2\text{-COMe}$ , b.p. 45–47°/25 mm., which, refluxed with  $\alpha\text{-C}_6\text{H}_4(\text{CO})_2\text{NK}$ , did not yield the corresponding amine. (I) with  $\text{AcCl}$  affords  $\beta$ -acetyl- $\beta$ -methylpentan- $\delta$ -one, b.p. 46–47°/15 mm. In attempts to prepare a SH analogue, (I) was saturated with  $\text{H}_2\text{S}$  at room temp. to yield a S-containing product, b.p. 36–42°/18 mm.; refluxed with  $\text{K}_2\text{S}_3\text{-C}_6\text{H}_6$ , (I) gives a product, b.p. 70–72°/22 mm., which is unsaturated, contains S, and, on degradation, yields  $\text{COMe}_2$ , S, and  $\text{Pr}^\beta\text{SH}$ .

II. Vals. of  $n_D^{20}$  (1.3929–1.3951) indicate that, when  $\text{COEt}_2$  is refluxed in presence of  $\text{Ba}(\text{OH})_2$ , polymerisation is not complete. Distillation after 100 hr. yields 34% of a product, b.p. 98°, 24°/27 mm., I val. 91–139 (*phenylurethane*, m.p. 232–233°;  *$\alpha$ -naphthylurethane*, m.p. 217°; *dinitrophenylsazone*, m.p. 148°). F. O. H.

**$\gamma$ -Ethylsulphonylbutan- $\beta$ -one and its bromo-derivatives.** L. Ramberg and B. Bäcklund (*Arkiv Kemi, Min., Geol.*, 1941, 15, A, No. 3, 22 pp.).— $\text{CHMeBr-COMe}$  (from Br and  $\text{COMeEt}$ ) and  $\text{EtSO}_2\text{Na}$  (I) in  $\text{EtOH}$  give (54% yield)  $\gamma$ -ethylsulphonylbutan- $\beta$ -one (II), m.p. –1.3°, b.p. 135°/8 mm. [*p*-nitrophenylhydrazone, A, orange plates, m.p. 138.8–139.4° (corr.), B, yellow needles, m.p. 133.5–134.5° (corr.); A  $\rightarrow$  B slowly at room temp., B  $\rightarrow$  A in several hr. above the m.p.]. (II) with hot dil.  $\text{KOH}$  gives  $\text{Et}_2\text{SO}_2$  (98% yield) and  $\text{KOAc}$ . (II) gives in  $\text{H}_2\text{O}$  or 1–2N- $\text{HBr}$  at room temp. with 1 mol. of Br (62% yield)  $\gamma$ -bromo- (III), m.p. 26.0–26.7°, b.p. 140–141°/8 mm., and with excess of Br (5–6 days; 80% yield)  $\alpha\alpha\gamma$ -tribromo- (IV), m.p. 131.9°, but in  $\text{EtBr}$  with 1 mol. of Br (64% yield)  $\alpha$ -bromo- $\gamma$ -ethylsulphonylbutan- $\beta$ -one (V), m.p. 66.3°, b.p. ~170°/8 mm. (III) rearranges to (V) at room temp. rapidly in presence of dry  $\text{HBr}$  > conc. aq.  $\text{HBr}$  >> conc. aq.  $\text{HCl}$  > alone (several months); dry  $\text{HCl}$  or  $\text{Bz}_2\text{O}_2$  has no effect, but the rearrangement is accelerated by ultra-violet light. (III) probably oxidises  $\text{HBr}$  to  $\text{Br}$ , which then brominates in the  $\alpha$ -position. (III) reacts with alkalis: (III) +  $4\text{OH}^- \rightarrow \text{cis}-(\text{CH}_2\text{-CH})_2 + \text{SO}_2^{2-} + \text{OAc}^- + \text{Br}^- + \text{H}_2\text{O}$  (cf. A., 1940, II, 335), but (V) gives  $\text{Et}_2\text{SO}_2$  and undergoes a complex decomp. (V) with (I) gives  $\alpha\gamma$ -bisethylsulphonylbutan- $\beta$ -one (VI), m.p. 65.3–65.9°, titratable as an acid ( $K_{25} = 4.07 \times 10^{-7}$ ), but decomposed by hot dil.  $\text{KOH}$  to  $\text{Et}_2\text{SO}_2$  and  $\text{EtSO}_2\text{-CH}_2\text{-CO}_2\text{K}$  (converted by  $\text{Br-KBr}$  into  $\text{EtSO}_2\text{-CHBr}_2$ ), with  $\text{PhSO}_2\text{Na}$  (VII)  $\alpha$ -phenylsulphonyl- $\gamma$ -ethylsulphonylbutan- $\beta$ -one, m.p. 95.6°, a stronger acid than (VI), and with  $\text{NaSPH}$  (VIII)

$\text{SO}_2\text{Et}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SPh}$  (not characterised), hydrolysed (hot dil. KOH) to  $\text{Et}_2\text{SO}_2$  (84%) and  $\text{SPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$ ; (I), (VII), and (VIII) are oxidised by (III) without coupling. (IV) oxidises KI,  $\text{SO}_2$ ,  $\text{N}_2\text{H}_4$ , etc., the  $\gamma$ -Br atom probably being reduced, but the  $\alpha\alpha\alpha$ -Br<sub>3</sub>-derivative could not be isolated. With alkali in MeOH at room temp. (IV) gives  $\text{SO}_2\text{Et}\cdot\text{CBrMe}\cdot\text{CO}_2$  (77% yield) and  $\text{CHBr}_3$  (60% yield). M. H. M. A.

**tert.-Alkyl primary amines,  $\text{CRR}'\text{R}''\cdot\text{NH}_2$ .** II. H. R. Henze, B. B. Allen, and W. B. Leslie (*J. Amer. Chem. Soc.*, 1943, 65, 87—89).—The abnormal reaction of  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{MgCl}$  (I) (2 mols.) with  $\text{OEt}\cdot\text{CH}_2\cdot\text{CN}$  (II) (1 mol.) to give a *tert.* amine (A., 1939, II, 409) is not confined to (II). Thus, the appropriate nitrile yields 30—59% of  $\alpha\alpha$ -diallyl- $\Delta^7$ -n-butenylamine [triallylcarbinylamine] (III), b.p. 182—183.5°/741 mm. (picrate, m.p. 173.5—174.5),  $\alpha\alpha$ -diallyl-n-butyl- (IV), b.p. 190—191°/742 mm. (picrate, m.p. 149—149.5°), and -n-amyl-amine, b.p. 205—206°/742 mm. (picrate, m.p. 121.5—122°),  $\alpha$ -benzyl-, b.p. 268.5° (decomp.)/742 mm. (picrate, m.p. 139.5—140°), and  $\alpha$ -n-butoxy-, b.p. 233—234°/742 mm. (picrate, m.p. 106.5—107°),  $\alpha$ -allyl- $\Delta^7$ -n-butenylamine.  $\text{OBu}^a\cdot\text{CH}_2\cdot\text{CN}$  (prep. from  $\text{CH}_2\text{Cl}\cdot\text{OBu}^a$  and  $\text{CuCN}$ ) (0.28), b.p. 79°/30 mm., with  $\text{MgBu}^a\text{Br}$  (0.28) and then (I) (0.37 mol.) in  $\text{Et}_2\text{O}$  gives  $\alpha$ -n-butoxymethyl- $\alpha$ -allyl-n-amylamine (54%), b.p. 247.5—248.5°/742 mm. (picrate, m.p. 79—80°).  $\text{H}_2$ -PtO<sub>2</sub> reduces (III) in  $\text{COMe}_2$  or (IV) in  $\text{EtOH}$  to  $\alpha\alpha$ -di-n-propyl-n-butylamine, b.p. 190.5—191.5°/742 mm. (picrate, m.p. 154—154.5°). Temp. are corr. R. S. C.

**Utilisation of aliphatic nitro-compounds. V. Reduction of nitroalcohols and -glycerols to the corresponding amines.** K. Johnson and E. F. Degering (*J. Org. Chem.*, 1943, 8, 7—9).—NO<sub>2</sub>-alcohols and -glycerols are unstable under most reducing conditions but are reduced to the corresponding NH<sub>2</sub>-compounds by catalytic hydrogenation (Raney Ni) with fair yields. Some decomp. causes the simultaneous formation of other bases. The method has been applied to the prep. of  $\beta$ -amino- $\beta$ -methyl-,  $\beta$ -ethyl-,  $\beta$ -n-propyl-, and  $\beta$ -isopropyl-propane- $\alpha$ -diol,  $\text{NH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ ,  $\text{NH}_2\cdot\text{CHEt}\cdot\text{CHMe}\cdot\text{OH}$ ,  $\text{NH}_2\cdot\text{CHEt}\cdot\text{CHBu}^a\cdot\text{OH}$ ,  $\text{NH}_2\cdot\text{CHEt}\cdot\text{CH}_3\cdot\text{OH}$ , and  $\text{NH}_2\cdot\text{CMeEt}\cdot\text{CH}_2\cdot\text{OH}$  (for details of these compounds see Vanderbilt and Hass, A., 1940, II, 62). H. W.

**Nature of Waser's specific colour reaction for  $\alpha$ -amino-acids.** P. Karrer and R. Keller (*Helv. Chim. Acta*, 1943, 26, 50—54; cf. A., 1924, i, 1068).—The intense blue-violet colour formed by the action of  $p$ -NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>·COCl (but not *o*- or *m*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>·COCl or BzCl) on  $\alpha$ -NH<sub>2</sub>-acids in presence of Na<sub>2</sub>CO<sub>3</sub> or, better, C<sub>5</sub>H<sub>5</sub>N is due to the alkali salts of the lactones of the *p*-nitrobenzamido-acids,  $\text{ONa}\cdot\text{N}=\text{C}_6\text{H}_4\cdot\text{C}(\text{O})\cdot\text{CH}(\text{CO})\cdot\text{N}(\text{Alk})$ . Agitation of a solution of *l*-leucine in 2N-NaOH with  $p$ -NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>·COCl in  $\text{Et}_2\text{O}$  gives *r*-N-*p*-nitrobenzoyl-leucine, m.p. 222—223°, and 2-*p*-nitrophenyl-4-isobutyloxazol-5-one (*p*-nitrobenzoyl-leucine lactone), m.p. 76°. H. W.

**Biological formation of acetylcholine.**—See A., 1943, III, 262.

**Magnetic behaviour of complexes of nitrilotriacetic acid, ethylenediaminetetra-acetic acid, and imines of salicylaldehyde.**—See A., 1943, I, 119.

**Manufacture and application of acid amide derivatives.**—See B., 1943, II, 72.

**Acrylonitrile. III. Cyanoethylation of  $\alpha\beta$ -unsaturated compounds.** IV. Cyanoethylation of active hydrogen groups. H. A. Bruson and T. W. Riener (*J. Amer. Chem. Soc.*, 1943, 65, 18—23, 23—27; cf. A., 1943, II, 122).—III.  $\text{CMeR}\cdot\text{CHX}$  (A) (X = COMe, CO·NH<sub>2</sub>, or CN) and  $\text{CH}_2\cdot\text{CH}\cdot\text{CN}$  (I) in presence of  $\text{CH}_2\text{Ph}\cdot\text{NMe}_3\cdot\text{OH}$  (II) or KOH give  $\text{CMeR}\cdot\text{CX}\cdot[\text{CH}_2]_2\cdot\text{CN}$  and, as main product, by rearrangement of (A),  $\text{CH}_2\cdot\text{CR}\cdot\text{CX}\cdot[\text{CH}_2]_2\cdot\text{CN}$  (B). (A) exists in equilibrium with  $\text{CH}_2\cdot\text{CR}\cdot\text{CH}_2\cdot\text{X}$  and equilibrium is disturbed by formation of (B). Adding (II) at 25° and then (I) at 5—10° to  $\text{CMe}_2\cdot\text{CH}\cdot\text{COMe}$  in Bu<sup>o</sup>OH gives  $\gamma$ -acetyl- $\gamma$ -isopropenylpimelodinitrile (III) (73.5%), m.p. 116—117°, and  $\delta$ -keto- $\gamma$ -isopropylidene-n-hexonitrile (10—15%), b.p. 110—115°/2 mm. [with (I) and (II) gives 50% of (III)]. In boiling, aq. KOH, (III) gives  $\gamma$ -acetyl- $\gamma$ -isopropylidenepimelic acid, m.p. 136—137°, which with  $\text{Ca}(\text{OCl})_2$ -KOC1-KOH-K<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O at 50° gives  $\text{CHCl}_3$  and  $\gamma$ -carboxy- $\gamma$ -isopropenyl-, m.p. 160°, hydrogenated (Raney Ni) as Na salt in H<sub>2</sub>O at 135°/115 atm. to  $\gamma$ -carboxy- $\gamma$ -isopropyl-pimelic acid (IV), m.p. 160°.  $\text{COMe}\cdot\text{CH}_2\text{Pr}^\beta$  with (I) and (II) in Bu<sup>o</sup>OH at 32—35° gives  $\gamma$ -acetyl- $\gamma$ -isopropylpimelodinitrile (poor yield), m.p. 101° (and much tar), converted, as above, into  $\gamma$ -acetyl- $\gamma$ -isopropylpimelic acid, m.p. 148°, and thence (IV) [proof of structure of (III) etc.].  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CN}$  (V) (1) with (I) (1 mol.) and (II) in Bu<sup>o</sup>OH at 10—15° (later room temp.) gives  $\gamma$ -cyano- $\gamma$ -vinylpimelodinitrile (VI), m.p. 60—61°, and a smaller amount of  $\gamma$ -cyano- $\Delta^7$ -n-hexenonitrile, b.p. 134—137°/10 mm. [with (I) and (II) in Bu<sup>o</sup>OH at 20—30° gives (VI)], hydrolysed to  $\gamma$ -carboxy- $\gamma$ -vinylpimelic acid (VII), m.p. 153°, and  $\text{CHMe}\cdot\text{C}(\text{CO}_2\text{H})\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ , m.p. 151—153° (lit. 152°). Hydrogenation of (VII) gives  $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_2)_2\cdot\text{CO}_2\text{H}$  (*loc. cit.*), m.p. 171—172°.  $\text{CHMe}\cdot\text{CH}\cdot\text{CN}$  gives the same products as does (V), proving the existence of the equilibrium.  $\text{CMe}_2\cdot\text{CH}\cdot\text{CN}$  (prep. by exothermic rearrangement of  $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CN}$  by (II) at 30—55°),

b.p. 140—142°, with (I) and (II) in Bu<sup>o</sup>OH at 30—40° gives  $\gamma$ -cyano- $\delta$ -methyl- $\Delta^7$ -n-hexenonitrile, b.p. 150°/10 mm., and  $\gamma$ -cyano- $\gamma$ -isopropylidenepimelodinitrile, m.p. 67—68° (hydrolysed by boiling 10% aq. NaOH to  $\gamma$ -cyano- $\gamma$ -isopropylidenepimelic acid, m.p. 167—168°). *cyclo*Hexylidenecetonitrile (prep. from *cyclo*hexanone,  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and C<sub>5</sub>H<sub>5</sub>N at 10—20° and later 100—105°), b.p. 105—110°/21 mm., with (I)-(II)-Bu<sup>o</sup>OH at 28—37° gives mainly  $\gamma$ -cyano- $\gamma$ - $\Delta^a$ -cyclohexenylpimelodinitrile, m.p. 81—82°.  $\text{CHMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$  with (I) and (II) in MeCN at 25—30° gives mainly  $\gamma$ -carbamyl- $\gamma$ -vinylpimelodinitrile, m.p. 77°, b.p. 235—240°/2 mm.

IV.  $\text{CH}_2$  in  $\text{CH}_2\text{Ar}\cdot\text{CN}$ ,  $\text{MeNO}_2$ ,  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{R}$ ,  $\text{CH}_2(\text{CO}\cdot\text{NH}_2)_2$ ,  $\text{CH}_2(\text{CO}_2\text{R})_2$ ,  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , or  $\text{CH}_2\text{Ar}\cdot\text{SO}_2\cdot\text{NH}_2$  is substituted by (I) in presence of strong alkali [(II) or 30% KOH-MeOH] in the solvent named below. Thus are obtained  $\gamma$ -nitro- $\gamma$ - $\beta'$ -cyanoethyl- (in dioxan; 25—35°), m.p. 114°,  $\gamma$ -cyano- $\gamma$ -phenyl- (in Bu<sup>o</sup>OH; 10—25°; 94%), m.p. 70°,  $\gamma$ -cyano- $\gamma$ -*p*-nitrophenyl- (in dioxan), m.p. 147—148°,  $\gamma$ -cyano- $\gamma$ -carbethoxy- (in dioxan; 30—35°; nearly 100%), m.p. 37°,  $\gamma\gamma$ -dicarbethoxy- (in dioxan; 30—35°; 82%), m.p. 62°,  $\gamma$ -cyano- $\gamma$ -carbamyl- (in H<sub>2</sub>O; 35—40°), m.p. 118°,  $\gamma\gamma$ -dicarbamyl- (in H<sub>2</sub>O; 35—38°), m.p. 210°, and  $\gamma$ -sulphonamido- $\gamma$ -phenyl-, m.p. 103—104°, -pimelodinitrile, *Et*  $\gamma$ -cyano- $\alpha$ -carbethoxy- $\alpha$ -ethyl-, m.p. 47°, and  $\alpha$ -benzyl-n-butyrate (in dioxan; 30—35°), m.p. 47°, b.p. 175—180°/1 mm., and *Et*  $\alpha$ -carbethoxy- $\alpha$ - $\beta'$ -cyanoethyl-n-hexoate (in dioxan; 30—35°), b.p. 145—150°/1 mm. OH-compounds give the  $\text{CN}\cdot[\text{CH}_2]_2$  ethers. Thus, the appropriate glycol with (I) and a little 40% aq. KOH or NaOMe at 25—35° gives 80—95% of ethylene, b.p. 158°/2 mm.,  $\alpha\beta$ -propylene, b.p. 165°/2 mm., trimethylene, b.p. 165°/1 mm.,  $\beta\gamma$ -butylene, m.p. 53—54°, b.p. 170°/2 mm., pentamethylene, b.p. 185°/1 mm., and decamethylene glycol di- $\beta$ -cyanoethyl ether, b.p. 225°/1 mm.,  $\beta\beta'$ -di-( $\beta'$ -cyanoethoxyethyl) ether, b.p. 190°/1 mm., and sulphide, b.p. 225°/2 mm., ethylene glycol di- $\beta$ - $\beta'$ -cyanoethoxyethyl ether, b.p. 215°/1 mm., and  $\alpha\beta\gamma$ -tri- $\beta'$ -cyanoethoxyethylpropane, b.p. 260°/1 mm. The appropriate oxime with (I) and NaOMe, NaOH, or (II) at 25—35° to 50—60° gives *acet*-, b.p. 85°/10 mm., *Me Et ket*-, b.p. 109°/21 mm., *acetophenone*-, m.p. 44°, and *furfurald-oxime*  $\beta$ -cyanoethyl ether, m.p. 116°, and *glyoxime*, m.p. 123°, and *benzoin oxime* di- $\beta$ -cyanoethyl ether, m.p. 72—73°. R. S. C.

**Manufacture of  $\alpha$ -cyano- $\Delta^7$ -butadiene.**—See B., 1943, II, 72.

## II.—SUGARS AND GLUCOSIDES.

**Diginin. II. Constitution of diginose.** C. W. Shoppee and T. Reichstein (*Helv. Chim. Acta*, 1942, 25, 1611—1623; cf. A., 1940, II, 336).—Diginonolactone,  $[\alpha]_D^{25} -29.8^\circ \pm 1^\circ$  in  $\text{COMe}_2$ , does not give cryst. derivatives with  $p$ -C<sub>6</sub>H<sub>4</sub>Br·NH·NH<sub>2</sub> or NPh<sub>2</sub>·NH<sub>2</sub> at 100°. It is transformed by successive treatments with Ba(OH)<sub>2</sub> and S-benzylthiuronium sulphate into S-benzylthiuronium diginonate, m.p. 137—138°,  $[\alpha]_D^{25} -9.2^\circ \pm 2^\circ$  in MeOH. The corresponding salts of cymaronic, sarmentonic, and oleandronic acid have m.p. 130—130.5°,  $[\alpha]_D^{25} 0^\circ \pm 2^\circ$  in MeOH, m.p. 46°,  $[\alpha]_D^{25} +6.5^\circ \pm 2^\circ$ ,  $[\alpha]_D^{25} +10.6^\circ \pm 2^\circ$ , and 128—130°,  $[\alpha]_D^{25} +5.8^\circ \pm 2^\circ$  in MeOH. A ready method for the differentiation of diginose (I), cymarose (II), sarmentose, and oleandrose is thus afforded. (II) is oxidised by KMnO<sub>4</sub> (=4 O) to AcOH and *l*(-)-methoxysuccinic acid, isolated as the diamide (III), m.p. 183—184°,  $[\alpha]_D^{25} -57.2^\circ \pm 2^\circ$  in MeOH. In the attempted prep. of (III) Me<sub>2</sub> *l*(-)-malate was treated successively with CH<sub>2</sub>N<sub>2</sub> (which did not cause methylation) and NH<sub>3</sub>, thus giving an unstable form, m.p. 149—150° after becoming opaque, of *l*(-)-maldiamide; it has  $[\alpha]_D^{25} -37^\circ \pm 2^\circ$  in H<sub>2</sub>O and solidifies to the stable variety, m.p. 162°. When oxidised similarly (I) yields AcOH and *d*(+)-methoxysuccinic acid, identified as the diamide, m.p. 183—184°,  $[\alpha]_D^{25} +56.8^\circ \pm 4^\circ$  in MeOH. (I) is most probably A. In acid medium (II) reacts relatively slowly with HIO<sub>4</sub> and does not give a well-defined end-point. (I) reacts more rapidly but consumes >1 O. In presence of K<sub>2</sub>CO<sub>3</sub> oxidation proceeds appreciably more rapidly whereby (II) consumes O uniformly up to 1 equiv. and then more slowly but without giving a sharp end-point whilst (I) consumes uniformly ~2 equivs., after which a slight retardation is observed. M.p. are corr. (block). H. W.

**Amino-aldehyde linkings.** G. Ågren and A. Taylor (*Arkiv Kemi, Min., Geol.*, 1941, 14, B, No. 14, 6 pp.).—*o*- or *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and glucose (I) in H<sub>2</sub>O at 70°, then at 0° for 12 hr., followed by evaporation in a vac., give compounds, C<sub>13</sub>H<sub>15</sub>O<sub>8</sub>N, m.p. 126° or 122°, respectively. Reaction with (I) is facilitated by using CO<sub>2</sub>Et·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>·HCl in H<sub>2</sub>O (evaporate rapidly in a vac. at 15°) thus affording compounds, C<sub>15</sub>H<sub>21</sub>O<sub>8</sub>NCl. It is probable that some azo-derivative is formed as a secondary reaction. Esterification of CO<sub>2</sub>H in NH<sub>2</sub>-acids and peptides facilitates reaction between NH<sub>2</sub> and CHO groups. A. T. P.

**Crystalline 4-methyl-D-mannose and its derivatives.** W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, 65, 70—73).—4-Methyl-2:3-isopropylidene-D-mannosan <1:5> $\beta$ <1:6 (I) and N-HCl at 100° give 4-methyl-D-mannose

(II), *α*-form, m.p. 127—128°,  $[\alpha]_D^{20} +34^\circ \rightarrow +22.6^\circ$  in  $H_2O$  ( $k$  0.020 at 20°) (*phenylhydrazone*, m.p. 158—159°,  $[\alpha]_D^{20} +46.2^\circ \rightarrow +17.8^\circ$  in  $C_6H_5N$  in 6 days; *phenyllosazone*, m.p. 157—158°,  $[\alpha]_D^{20} -36^\circ \rightarrow -14.4^\circ$  in  $C_6H_5N$  in 24 hr.). With boiling dry 3% HCl-MeOH, (I) gives *α*-methyl-4-methyl-D-mannopyranoside (55%), m.p. 101—102°,  $[\alpha]_D^{20} +83.9^\circ$  in  $H_2O$  [in 0.05N-HCl gives (II)]. (II) gives *tetraacetates*, m.p. 75—76°,  $[\alpha]_D^{20} +59.2^\circ$  in  $CHCl_3$ , and m.p. 63—64°,  $[\alpha]_D^{20} +20.2^\circ$  in  $CHCl_3$ . Br-CaCO<sub>3</sub>-H<sub>2</sub>O gives 4-methyl-D-mannono- $\delta$ -lactone, m.p. 165—166°,  $[\alpha]_D^{20} +163.8^\circ \rightarrow +94.2^\circ$  in  $H_2O$  in 6 days, and thence 4-methyl-D-mannono-phenylhydrazide, m.p. 146—147°,  $[\alpha]_D^{20} +10.6^\circ$  in  $H_2O$ , and -amide, m.p. 171—172°,  $[\alpha]_D^{20} +11.9^\circ$  in  $H_2O$  (1:2:3:5:6-penta-acetate, m.p. 98—99°,  $[\alpha]_D^{20} +11.4^\circ$  in  $CHCl_3$ ). H<sub>2</sub>-Raney Ni in  $H_2O$  at 100°/167 atm. gives 4-methyl-D-mannitol, m.p. 86—87° (foams), resolidifies, remelts at 133—134°,  $[\alpha]_D^{20} +16.7^\circ$  in  $H_2O$  [penta-acetate, m.p. 85—86°,  $[\alpha]_D^{20} +35.4^\circ$  in  $CHCl_3$ ; (CMe<sub>2</sub>)<sub>2</sub> derivative, m.p. 57—58°,  $[\alpha]_D^{20} +9.0^\circ$  in EtOH]. Relations of (II) to D-mannose are discussed.  $[\alpha]_D^{20}$  are  $[\alpha]_D^{20}$ .

R. S. C.

**Synthesis of amino-sugars.** I. W. H. Myers and G. J. Robertson (*J. Amer. Chem. Soc.*, 1943, 65, 8—11).—Aminoglucosides are prepared by ring-fission of benzylidene-2:3-anhydroglucosides by NH<sub>3</sub>, two *trans*-isomerides being formed, of which one is in large excess (cf. Peat *et al.*, A., 1939, II, 7). 4:6-Benzylidene-2:3-anhydro- $\alpha$ -methylalloside and conc. aq. NH<sub>3</sub> at 100° (sealed tube) give mixed NH<sub>2</sub>-derivatives (A) (100%), m.p. 168°,  $[\alpha]_D^{18} +104.7^\circ$  in  $CHCl_3$ , whence Ac<sub>2</sub>O-C<sub>5</sub>H<sub>5</sub>N yields 60% of 2-acetamido-4:6-benzylidene- $\alpha$ -methylaltroside 3-acetate (I) (cf. *loc. cit.*). With boiling 0.5% HCl-MeOH, (I) gives 2-acetamido- $\alpha$ -methylaltroside 3-acetate (60%), m.p. 189° (decomp.),  $[\alpha]_D^{18} +7.3^\circ$  in MeOH, and with boiling Ac<sub>2</sub>O-NaOAc gives the corresponding triacetate (II) (65%), m.p. 176°,  $[\alpha]_D^{20} +110^\circ$  in  $CHCl_3$ . With conc. HCl in cold CMe<sub>2</sub>, (A) give 2-amino-4:6-benzylidene- $\alpha$ -methylaltroside hydrochloride, m.p. 96°,  $[\alpha]_D^{21} +85.5^\circ$  in  $CHCl_3$ . 4:6-Benzylidene-2:3-anhydro- $\alpha$ -methylmannoside and conc. aq. NH<sub>3</sub> at 100° give a mixture (B), m.p. 188°,  $[\alpha]_D^{19} +88.9^\circ$  in  $CHCl_3$ , separated by acetylation into 3-acetamido-4:6-benzylidene- $\alpha$ -methylaltroside 2-acetate (III) (60%), m.p. 201°,  $[\alpha]_D^{12} +14.6^\circ$  in  $CHCl_3$ , and 2-acetamido-4:6-benzylidene- $\alpha$ -methylglucoside 3-acetate (1%), m.p. 235°,  $[\alpha]_D^{12} +45.5^\circ$  in  $CHCl_3$ . With conc. HCl in CMe<sub>2</sub>, (B) gives 3-amino-4:6-benzylidene- $\alpha$ -methylaltroside hydrochloride (88%), m.p. 183° (decomp.),  $[\alpha]_D^{19} +83.5^\circ$  in  $H_2O$ . With 0.5% HCl-MeOH at 55°, (III) gives 3-acetamido- $\alpha$ -methylaltroside 2-acetate (60%), m.p. 174°,  $[\alpha]_D^{16} +106.2^\circ$  in  $CHCl_3$ , which by acetylation gives the triacetate (IV), m.p. 177°,  $[\alpha]_D^{18} +34.1^\circ$  in  $CHCl_3$ . With 2N-HCl (19 c.c.) in boiling  $H_2O$  (400 c.c.), (A) gives, according to the method, 2-amino- $\alpha$ -methylaltroside, m.p. 193°,  $[\alpha]_D^{20} +107^\circ$  in  $CHCl_3$ , or its hydrochloride, a syrup,  $[\alpha]_D^{22} +39.7^\circ$  in  $CHCl_3$ . In boiling 1% HCl, (B) gives 3-amino- $\beta$ -methylaltroside hydrochloride (=methylepiglucoamine hydrochloride), m.p. 209° (decomp.),  $[\alpha]_D^{18} -149^\circ$  in  $H_2O$ . 2:3-Anhydro- $\alpha$ -methylalloside and NH<sub>3</sub> give a syrup whence 68% of (II) is obtained. 4:6-Benzylidene-2:3-anhydro- $\alpha$ -methylmannoside and boiling aq. H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> give 2:3-anhydro- $\alpha$ -methylmannoside (80%), m.p. 67°,  $[\alpha]_D^{20} +44.6^\circ$  in  $CHCl_3$ , which with NH<sub>3</sub> gives a syrup, yielding (IV) (65%) and 2-acetamido- $\alpha$ -methylglucoside triacetate, m.p. 132°,  $[\alpha]_D^{20} +44.6^\circ$  in  $CHCl_3$ . 2-Amino-4:6-benzylidene- $\beta$ -methylglucoside and Ac<sub>2</sub>O-C<sub>5</sub>H<sub>5</sub>N give the N-Ac derivative 3-acetate (75%), m.p. 158°,  $[\alpha]_D^{20} -12.9^\circ$  in  $CHCl_3$ , which with NH<sub>3</sub> gives a syrup and thence 2-acetamido- $\beta$ -methylglucoside triacetate (70%), m.p. 238° (decomp.). 4:6-Benzylidene-2:3-anhydro- $\alpha$ -methylguloside (or -taloside) and NH<sub>3</sub> give a mixture (80%), m.p. 128—130°,  $[\alpha]_D^{20} +60.6^\circ$  in  $CHCl_3$ , yielding 2- (or 3-)acetamido-4:6-benzylidene- $\alpha$ -methyl-idoside 3- (or 2-)acetate (V) (55%), m.p. 188°,  $[\alpha]_D^{19} +43.4^\circ$  in  $CHCl_3$ , and -galactoside 3- (or 2-)acetate (8%), m.p. 260°,  $[\alpha]_D^{12} +70.3^\circ$  in  $CHCl_3$ . Warm HCl converts (V) into 2- (or 3-)acetamido- $\alpha$ -methyl-idoside 3- (or 2-)acetate (81%), a syrup,  $[\alpha]_D^{18} -36.0^\circ$  in MeOH.

R. S. C.

**Alkaline degradation of phenylglucosides.** New method for determining the configuration of glucosides and sugars. (Miss) E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, 65, 3—7).— $\beta$ -Phenylglucosides etc. are degraded to anhydro-compounds by alkali much faster than are the  $\alpha$ -isomerides, thus confirming existing allocations of structure and affording a method of determining structures of arylglucosides and compounds with which they can be correlated.  $\beta$ -Phenyl-D-glucoside is completely hydrolysed by 1.3N-Ba(OH)<sub>2</sub> or -KOH at 100° in 9 hr., yielding 88% of D-glucosan <1:5> $\beta$ <1:6> (I), whereas 85% of the  $\alpha$ -isomeride is recovered after boiling for 2 weeks in 2.6N-KOH, there having been no change in  $[\alpha]$ .  $\beta$ -Phenyl-D-galactoside in 1.3N-KOH at 98° gives 91% of D-galactosan <1:5> $\beta$ <1:6> (II) in 9 hr.; 4% of the  $\alpha$ -galactoside is recovered after 16 weeks in 2.6N-KOH at 100° whilst 97% of PhOH (determined by I) is liberated, yielding 85% of (II).  $\alpha$ -Phenyl-D-mannoside in boiling 1.3N-KOH gives a syrup, whence a little D-mannosan <1:5> $\beta$ <1:6> is isolated as CMe<sub>2</sub> derivative, whereas the  $\beta$ -mannoside gives 57% (A., 1942, II, 351).  $\alpha$ -Phenyl-D-xyloside is unaffected, whereas the  $\beta$ -xyloside gives a decomposed syrup.  $\beta$ -o-Tolyl-,  $\beta$ -o-hydroxy-methylphenyl-,  $\beta$ -p-xenyl-,  $\beta$ -p-acetylphenyl-,  $\beta$ -o- (stable form, m.p. 168—169°; tetra-acetate, new m.p. 160—162°) and  $\beta$ -p-nitrophenyl-D-glucoside give 60—90% of (I), but  $\alpha$ - +  $\beta$ -methyl-,  $\beta$ -cyclohexyl-,

$\beta$ -n-decyl-, and  $\beta$ -allyl-glucosides are unchanged and the  $\alpha$ -o- and  $\alpha$ -p-nitrophenylglucosides give tars.

R. S. C.

**Synthesis of  $\beta\beta\beta$ -trichloroethyl-D-glucoside, and its isolation from maize and dandelion plants treated with chloral hydrate.** L. P. Miller (*Contr. Boyce Thompson Inst.*, 1942, 12, 465—470).— $\beta\beta\beta$ -Trichloroethyl-D-glucoside, m.p. 152.5—153.5° (corr.),  $[\alpha]_D^{25} -39.7^\circ$  in  $H_2O$  [from the synthetic tetra-acetate with Ba(OMe)<sub>2</sub> in MeOH], is isolated as tetra-acetate from the tops and roots of maize or dandelion grown in a medium containing CCl<sub>3</sub>·CH(OH)<sub>2</sub>, or directly, by Pb pptn. and Et<sub>2</sub>O extraction of aq. extracts, from the leaves of dandelion so grown, together with a trichloroethylglycoside isolated as the hexa-acetate, C<sub>25</sub>H<sub>33</sub>O<sub>15</sub>Cl<sub>3</sub>, m.p. 158—159° (or 170—171° after partial melting and resolidification),  $[\alpha]_D^{25} -47.2^\circ$  in  $CHCl_3$ .

A. LI.

**Steroids. XXXIV. Saccharides of deoxycorticosterone.** K. Miescher and C. Meystre (*Helv. Chim. Acta*, 1943, 26, 224—233).—Gradual addition of acetobromo-D-galactose in  $CHCl_3$  to a mixture of Ag<sub>2</sub>CO<sub>3</sub> and deoxycorticosterone (I) in this solvent at 40—45° followed by hydrolysis (K<sub>2</sub>CO<sub>3</sub> in MeOH) of the non-cryst. tetra-acetate gives deoxycorticosterone- $\beta$ -D-galactoside, m.p. 195—198°,  $[\alpha]_D^{20} +136^\circ \pm 4^\circ$  in CMe<sub>2</sub>. Under similar conditions but with C<sub>6</sub>H<sub>6</sub> as solvent acetobromolactose yields deoxycorticosterone- $\beta$ -lactoside, m.p. 202—208°,  $[\alpha]_D^{20} +80^\circ \pm 4^\circ$  in MeOH (hepta-acetate, m.p. 194—195°,  $[\alpha]_D^{20} +52^\circ \pm 4^\circ$  in CMe<sub>2</sub>). Deoxycorticosterone-maltoside hepta-acetate has m.p. 183—185°. (I) is shaken with acetobromolactosido-D-glucose and Ag<sub>2</sub>CO<sub>3</sub> in  $CHCl_3$  at 40—45° and the product is transformed by Ac<sub>2</sub>O-C<sub>5</sub>H<sub>5</sub>N into the hendeca-acetate, m.p. (indef.) 120—130°, of deoxycorticosterone-6- $\beta$ -lactosido-D-glucoside (+2H<sub>2</sub>O), m.p. (indef.)  $\sim 160^\circ$ . 6- $\beta$ -Lactosido-D-glucose hendeca-acetate, m.p. 192—194°, is obtained by shaking glucose tetra-acetate with acetobromolactose and CaCl<sub>2</sub> in EtOH-free  $CHCl_3$  and continuing the process after addition of Ag<sub>2</sub>CO<sub>3</sub> and I; it is converted by HBr-AcOH into 6- $\beta$ -lactosidoacetobromo-D-glucose hepta-acetate, m.p. 138—142°. The prep. of permanent supersaturated 1% and 2% aq. solutions of deoxycorticosterone- $\beta$ -D-glucoside is described; this compound is less freely sol. in  $H_2O$  than are the new saccharides. M.p. are corr.

H. W.

**Cerberin and cerberoside.**—See A., 1943, III, 343.

**Starch. XXIV. Composition of various starches.** K. H. Meyer and P. Heinrich (*Helv. Chim. Acta*, 1942, 25, 1639—1650; cf. A., 1942, II, 303).—Extraction of starch (I) with  $H_2O$  at a suitable temp. (between 50° and 80°) which must be determined for each variety causes dissolution solely of amylose (II) since the sol. portion does not give residual dextrin (III) when degraded by  $\beta$ -amylase (IV); at a higher temp. the branched components also pass into solution and yield (III). Treatment of (I) with boiling  $H_2O$  followed by electrodialysis brings the greater part of the amylopectin (V) to the anode side but part remains dissolved; the proportion increases with the temp. of extraction. Complete elimination of (II) is effected by solubilising (I) in conc. CaCl<sub>2</sub> and removing the salt by dialysis. After electrodialysis of the solution thus obtained the greater part of the branched components is deposited on the anodic side. A great part of the polysaccharides, certainly containing all of (II), remains in solution. Evidence is brought in favour of the view that the main part of this dissolved fraction is a slightly ramified (V) of low mol. wt.; this is termed the "intermediate fraction." The results of the examination of starches from maize, rice, tubers, leaves, and shoots of potatoes, sago, tapioca, and peas are tabulated. (I) from rice contains a small proportion of a freely sol. polysaccharide of low mol. wt. giving 52% of (III) when degraded by (IV). The principal part of the grain is composed of a very sparingly sol. polysaccharide which scarcely swells and should therefore have a very high mol. wt.; it gives 42% of (III). A similar variety of (I) occurs in "waxy maize."

H. W.

**Application of the mercaptalation assay to synthetic starch.** M. L. Wolfrom, C. S. Smith, and A. E. Brown (*J. Amer. Chem. Soc.*, 1943, 65, 255—259).—Synthetic starch (prep. from  $\alpha$ -, not  $\beta$ -, glucopyranose 1-phosphate by potato phosphorylase) is hydrolysed by conc. HCl at 0° in presence of EtSH.  $k$  (determined by  $[\alpha]$ ) for depolymerisation is 0.032 hr.<sup>-1</sup> (cf. 0.027 for natural potato starch). The initial average degree of polymerisation is  $32 \pm 1$  glucose units.

R. S. C.

**Multiple amylose concept on starch. III. Isolation of an amylose in crystalline form.** R. W. Kerr and G. M. Severson (*J. Amer. Chem. Soc.*, 1943, 65, 193—198; cf. A., 1942, II, 219).—Attempts to isolate  $\gamma$ -amylose (I) from the fraction of maize starch (II) less sol. in EtOH failed. Fractionation of potato starch (III) by aq. EtOH reveals a greater solubility and smaller tendency to gel, compared with (II). Extraction of (II) by  $H_2O$  at < the gelatinisation temp. gives a solution [5.1% of the (II) dissolved], which at 0° deposits 94% of its solids as a gelatinous mass but with a little BuOH it deposits 79.5% of its solids as a cryst. amylose (photo-micrograph). The amorphous ppt. has a conversion limit (barley diastase) 86% and alkali no. 35.4. Cryst. amylose has a conversion limit 93% and alkali no. 35.0, gives a purple colour with I and a very sharp "V" type X-ray pattern, and contains essentially linear 1:4- $\alpha$ -glucosidically linked glucopyranose units. (III) yields

a similar, but crystallographically slightly different, cryst. amylose, having conversion limit 97% and alkali no. 21.3. The conversion limit of (I) is raised to 70% by working in more dil. solution. The part (~25%) of whole (II) pptd. by BuOH has alkali no. 22 and conversion limit 81%. Cryst. amylose is part of the starch ingredients adsorbed on cotton. It is concluded that starch contains amylose varying from the almost wholly linear to fairly highly branched, the proportion of the latter being higher in (III) than in (II). R. S. C.

**Significance of the degradation of starch by macerans amylase.** R. W. Kerr (*J. Amer. Chem. Soc.*, 1943, **65**, 188—193).—Gelatinisation of dioxan-extracted maize starch in aq. NaOH and treatment with *B. macerans* amylase (I) at 45° and pH 6 gives 9.9% of insol. matter (resembling  $\gamma$ -amylose) and a further ~0.3% when kept, and then by pptn. by  $C_2H_5Cl_3$  etc. 25.2—25.3% of mixed dextrans, in which the  $\beta$ : $\alpha$ -dextrin ratio is 0.26. Potato starch gives similarly first only 0.43% and then ~0.3% of insol. matter and 30.6% of mixed dextrans, in which the  $\beta$ : $\alpha$  ratio is 0.28. The mixed dextrans are unaffected by barley diastase. Hydrolysis of maize starch by acid progressively decreases the amount of insol. matter and rapidly that of the dextrans obtained by later treatment with (I). Limit dextrans, prepared by barley diastase, give no Scharinger dextrans by treatment with (I). The fraction (55%) of starch more sol. in aq. EtOH gives 43.6% of cryst. dextrans. It is concluded that these dextrans are formed enzymically by rearrangements of simpler configurations. R. S. C.

**Action of macerans enzyme on a component of maize starch.**—See A., 1943, III, 427.

**Amylose and amylopectin content of starches determined by their iodine complex formation.** F. L. Bates, D. French, and R. E. Rundle (*J. Amer. Chem. Soc.*, 1943, **65**, 142—148).—Potentiometric titration of amylose (I) (dispersed in alkali) with I-KI shows complex formation, followed by adsorption; amylopectin shows only adsorption. The following (I) contents of the starches are thus determined: waxy rice, waxy sorghum, waxy maize, waxy barley 0; tapioca, rice 17; banana 20.5; maize 21; potato 22; popcorn 23; wheat 24; sago 27; lily bulb 34%. These results agree with those obtained by pptn. by BuOH. The amount of I bound by (I)  $\propto$  inversely [I]. The affinity for I probably increases with the length of the straight chains and decreases with the degree of branching. The (I) of any one starch is probably homogeneous but is different for different starches. Hassid's synthetic starch (A., 1943, II, 25) is essentially (I). R. S. C.

**Diffraction of electrons in cellulose ethers and esters.**—See A., 1943, I, 146.

**Simplified preparation of Schweitzer's reagent.** A. Breslau (*J. Chem. Educ.*, 1942, **19**, 356). L. S. T.

### III.—HOMOCYCLIC.

**Thallos salts as derivatives of sulphonic acids.** H. Gilman and R. K. Abbott, jun. (*J. Amer. Chem. Soc.*, 1942, **65**, 123—124).—TI sulphonates are useful for identification, being readily prepared from the acid by TIOH (titration) or from the Na salt by  $HCO_2TI$  in approx. quant. yield and giving large crystals of high m.p. *TI sulphamate*, m.p. 139—140°, *sulphanilate*, m.p. 207—209°, *o*-, m.p. 213—216°, and *p*-toluene-, m.p. 226—228°, *p*-bromobenzene-, m.p. 274—276°, *m*-nitrobenzene-, m.p. 307—309°, *2*-bromotoluene-4-, m.p. 220—222°, *o*-toluidine-4-, m.p. 101—103°, *1*:*2*-naphthaquinone-4-, m.p. 228—232° (decomp.), *d*-camphor-, m.p. 267—269°, *1*:*2*:*3*:*4*-tetramethylbenzene-5-, m.p. 260—262° (very sol.), *1*:*2*:*3*:*5*-tetramethylbenzene-4-, m.p. 283—285° (fairly sol.), and *1*:*2*:*4*:*5*-tetramethylbenzene-3-, m.p. 340—341° (decomp.) (insol. in  $H_2O$ ), and *pentamethylbenzene*-, m.p. 325—326°, -sulphonate are described. R. S. C.

**Preparation of aromatic sulphonyl fluorides.**—See B., 1943, II, 70.

**Phenylmethanesulphinic acid.** B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1940, **14**, A, No. 8, 13 pp.).— $\beta$ -Benzylsulphonyl-propionic, m.p. 177—178°, and -succinic, m.p. 193—194°, acids, and  $CH_2Ph \cdot SO_2 \cdot CHMe \cdot CH_2 \cdot CO_2H$ , are hydrolysed (N-NaOH, 100°) via the  $HgCl$  salt to  $CH_2Ph \cdot SO_2H$  (I), m.p. 61—63°, and the appropriate unsaturated acid, the reaction being reversed in acid solution. (I) is stable to hot N-NaOH and cold. conc. HCl, and contrary statements (A., 1880, 811; 1906, i, 819) are due to its great sensitivity to atm.  $O_2$ . (I) with Br-AcOH gives *benzylsulphonyl bromide*, m.p. 79—80°. Chlorination of  $CH_2Ph \cdot CNS$  in  $H_2O$  (cf. A., 1939, II, 498) gives solutions containing only traces of (I).

M. H. M. A.

**Bromination of diphenylalkanes and preparation of stilbene derivatives.** II.  $\beta\gamma$ -Diphenyl-*n*-butane. H. J. Barber, R. Slack, and A. M. Woolman (*J.C.S.*, 1943, 99—101; cf. A., 1943, II, 92).— $CHPhMeCl$  and  $Mg-Et_2O$  give *meso*-(I), m.p. 124°, and *r*-( $CHPhMe$ )<sub>2</sub> (II), b.p. 153—156°/14 mm. (I) and Br in 95% AcOH afford 4:4': $\beta\gamma$ -tetrabromo- (III), m.p. 178—185° (de-

comp.), and *meso*-4:4'-dibromo- $\beta\gamma$ -diphenyl-*n*-butane (IV), m.p. 160—161°. The mother-liquors from (II) and Br-95% AcOH, after separation of (III), are diluted with  $H_2O$ , treated with Zn dust, and the product is hydrogenated ( $PtO_2$ ; 50 lb. per sq. in.) to dl-4:4'-dibromo- $\beta\gamma$ -diphenyl-*n*-butane (V), b.p. 166—171°/0.3—0.4 mm. A low yield of (IV) is obtained from *p*- $C_6H_4Br \cdot CHMeCl$  and Na- $C_6H_5$  (no reaction with  $Mg-Et_2O$ ). Unsuccessful attempts were made to dehydrogenate the 4:4'-Br<sub>2</sub>-compound with Pd-C at 300° or Cu chromite in  $PhNO_2$ , or to reduce (III) with CuCl in  $C_5H_5N$  or CuCN in quinoline, but (III) and Zn-AcOH (15 min.) readily yield *cis*-(VI), m.p. 90—92°, and *trans*-4:4'-dibromo- $\alpha\beta$ -dimethylstilbene (VII), m.p. 125—128°, both of which are oxidised by  $CrO_3$ -AcOH to *p*- $C_6H_4Br \cdot CO_2H$ . (VI) is converted into (VII) in boiling  $PhNO_2$ -I (trace). (VI) and  $HBr-CHCl_3$  at 0° afford 4:4': $\beta$ -tribromo- $\beta\gamma$ -diphenyl-*n*-butane, m.p. 112—115° (decomp.), converted at 150—200° (10 min.) into (VII). Hydrogenation ( $Pt$ ;  $COMe_2$ ) of (VI) [(VII) is not similarly reduced] affords (IV); addition of 2 Br gives (III). (IV) or (V) and CuCN- $C_5H_5N$  at 190—205° give *meso*-, m.p. 196—198°, or dl-4:4'-dicyano- $\beta\gamma$ -diphenyl-*n*-butane, b.p. 190—200°/1 mm., respectively. (VII) and CuCN in quinoline yield 4:4'-dicyano- $\alpha\beta$ -dimethylstilbene, sublimes at 240°/1 mm., m.p. 216°. *meso*-(dihydrochloride, + $H_2O$ ) and *r*-4:4'-diamidino- $\beta\gamma$ -diphenyl-*n*-butane (dihydrochloride, + $2H_2O$ ), are obtained in the usual manner through the iminoether hydrochloride. A. T. P.

**The ascorbic acid-dehydroascorbic acid system in synthesis and inactivation of sympathomimetic amines.** K. H. Beyer (*J. Pharm. Exp. Ther.*, 1942, **76**, 149—155).—Various amines were oxygenated at pH 7 in presence of ascorbic acid for 18—24 hr. Solutions were made basic and  $NH_3$  was determined. Those having no OH group in the ring and  $NH_2$  in the side-chain were deaminated with recovery of 30—54% of theoretical yield of  $NH_3$ . Side-chain OH  $\beta$  to  $NH_2$  decreased deamination to ~10%.  $NHMe$  in addition to side-chain OH did not affect deamination as compared with the corresponding primary amine; a *tertiary* amine did not undergo deamination. *p*-OH-amines were oxidised to the 3:4-(OH)<sub>2</sub>-compounds. V. J. W.

**Properties of *p*-hydroxylaminobenzenesulphonamide and a related molecular complex.** M. G. Sevag (*J. Amer. Chem. Soc.*, 1943, **65**, 110—113).— $p$ - $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$  and Zn dust in aq.  $NH_4Cl$  give  $p$ -OH- $NH \cdot C_6H_4 \cdot SO_2 \cdot NH_2$  (I), m.p. 141.5° (cf. Bratton *et al.*, A., 1940, III, 436), and a substance, m.p. 161.5° (cf. Burton, A., 1941, II, 220), shown to be a 2:1 complex of (I) and  $p$ - $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$  (II) by analysis, solubility, absorption of  $O_2$ , colorimetric determination of (II), and isolation of (II) as sulphate and hydrochloride. R. S. C.

*p*-Aminobenzenesulphonylcyanamide.—See B., 1943, II, 145.

**Azo-compounds and their intermediate products.** XXIII. *o*-(Benzeneazo)azobenzene. P. Ruggli and J. Rohner (*Helv. Chim. Acta*, 1942, **25**, 1533—1542; cf. A., 1938, II, 318).—Gradual addition of solid  $PhNO$  to  $o$ - $NH_2 \cdot C_6H_4 \cdot N_2Ph$  (prep. from  $o$ - $NO_2 \cdot C_6H_4 \cdot NH_2$  described) in cold AcOH gives *o*-(benzeneazo)azobenzene (I), m.p. 106—108°, in 83% yield; it is converted by reductive fission into  $o$ - $C_6H_4(NH_2)_2$  and  $NH_2Ph$ . (I) and  $CPh_2 \cdot CO$  in light petroleum or preferably in  $C_6H_6$  in presence or absence of light afford an adduct,  $C_{32}H_{24}ON_4$ , m.p. 162—163°. (I) is reduced by Zn dust and  $NH_3$ -EtOH to *o*-benzeneazohydrazobenzene (II), m.p. 98.5—100°, converted by  $H_2$ - $PtO_2$ -EtOH into  $o$ - $C_6H_4(NH_2)_2$  and  $NH_2Ph$ . Cryst. (II) is stable in air but in  $C_5H_5N$  is slowly dehydrogenated to (I). (II) is transformed by boiling AcOH under  $N_2$  into (I) and 2-phenylbenzotriazole (III). Addition of (II) to  $Ac_2O$  in  $Et_2O$  gives the *Ac* derivative,  $o$ - $PhN_2 \cdot C_6H_4 \cdot NH \cdot NPhAc$ , m.p. 102—103.5°, which passes at 180—200° into (III) and  $NHPhAc$ . (I) is reduced by Zn dust in  $C_5H_5N$ -conc. aq.  $NH_3$  to *o*-(phenylhydrazino)hydrazobenzene, m.p. 132° (yellow-orange at 122° and softens at 128°). It is rapidly dehydrogenated to (I) by air in  $C_5H_5N$ , disproportionated in  $CO_2$  to  $NH_2Ph$  and  $o$ - $NH_2 \cdot C_6H_4 \cdot N_2Ph$ , and converted by  $Ac_2O$  at 70° into *o*- $NHAc \cdot C_6H_4 \cdot N_2Ph$ . H. W.

**Action of cuprous oxide on diazotised amines.** II. Reactions in solutions of various alcohols and organic solvents. Preparation of 1:6-dinitronaphthalene. H. H. Hodgson and H. S. Turner (*J.C.S.*, 1943, 86—89; cf. A., 1943, II, 59).—1:6-2-( $NO_2$ )<sub>2</sub> $C_{10}H_5 \cdot N_2HSO_4$  [from the 2-*p*-toluenesulphonamide (improved prep.) and conc.  $H_2SO_4$  at 30—40°, followed by  $NO \cdot SO_3H$  and then AcOH at <20°] with EtOH yields 21, with  $Cu_2O$  18, but with  $Cu_2O$  in MeOH, EtOH,  $Pr^aOH$ ,  $Pr^bOH$ ,  $Bu^aOH$ ,  $Bu^bOH$ ,  $(CH_2OH)_2$ ,  $Cl[CH_2]_2OH$ ,  $COMe_2$ , and EtOAc yields 60.2, 57.6, 40.6, 59.7, 30, 51.2, 48.3, 69.5, 35.5, and 39.8%, respectively, of 1:6- $C_{10}H_6(NO_2)_2$  (I).  $CH_2Ph \cdot OH$ ,  $Bu^aOH$ , and cyclohexanone give no isolable product. 2:4:1-( $NO_2$ )<sub>2</sub> $C_{10}H_5 \cdot N_2HSO_4$  with  $Cu_2O$  in  $Cl[CH_2]_2OH$  gives 75% of 1:3- $C_{10}H_6(NO_2)_2$ . For the more anionoid alcohols an appreciable induction period occurs before a rapid decomp., suggesting a two-stage reaction, viz., complex formation between  $ArN_2X$  and org. solvent, followed by decomp. facilitated by  $Cu_2O$ . Prep. of (I), m.p. 166.5° (lit. 161°, 166—167°), is improved. A. Li.

**Amino-aldehyde linkings.**—See A., 1943, II, 154.

**Tautomerism of benzoquinone-*p*-nitrosophenol systems. II. 3-Fluoro-4-nitrosophenol.** H. H. Hodgson (*J.C.S.*, 1943, 89—90; cf. A., 1937, II, 251).—The ultra-violet absorption spectrum of 1 : 3 : 4-OH·C<sub>6</sub>H<sub>3</sub>F·NO (I) has unique features in comparison with those of its 3-halogeno-analogues (A). There is only one band (eliminated by acid; intensified by alkali), with peak at 3700 Å. Compared with (A) there is a large displacement of the band towards shorter λ; this supports the fact that (I), unlike (A), is not convertible into a quinonoid isomeride.

A. T. P.

**Amine-formaldehyde condensation in the formation of aniline-formaldehyde resins and of aminoplastics. I.** H. von Euler and H. Nyström (*Arkiv Kemi, Min., Geol.*, 1941, 14, B, No. 26, 7 pp.).—Partly an account of work previously abstracted (A., 1942, II, 309). 2 : 3 : 5 : 1-OH·C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·CH<sub>2</sub>·OH and NH<sub>2</sub>Ph·HCl in boiling aq. HCl (pH 2) give 4 : 6-dimethyl-2-anilinomethylphenol, m.p. 85° (N-NO-derivative, m.p. 118.5°) (2-*p*-toluidino-analogue, m.p. 99°), also obtained from 2 : 3 : 5 : 1-OH·C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·CH<sub>2</sub>Br and NH<sub>2</sub>Ph in PhMe. 1 : 4 : 2 : 3 : 5 : 6-(OH)<sub>2</sub>C<sub>6</sub>(CH<sub>2</sub>·OH)<sub>4</sub> (I) and boiling aq. NH<sub>2</sub>Ph·HCl, followed by boiling 4*N*-HCl, give an amorphous condensation product formed from 2 mols. of NH<sub>2</sub>Ph and 1 mol. of (I).

A. T. P.

***p*-Toluidine salts of monoaryl sulphates.** A. D. Barton and L. Young (*J. Amer. Chem. Soc.*, 1943, 65, 294—295).—KArSO<sub>4</sub> and *p*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>·HCl in H<sub>2</sub>O give *p*-C<sub>6</sub>H<sub>4</sub>Me·NH Ph, m.p. 145—146°, o-, m.p. 135.5—136.5°, m-, m.p. 133—134°, and *p*-tolyl, m.p. 162—163°, *p*-bromophenyl, m.p. 193—194°, and *p*-nitrophenyl sulphate, m.p. 167—168° (cf. Burkhardt *et al.*, A., 1926, 511).

R. S. C.

**Chlorination of *p*-diphenyl acetate in acetic acid.** H. R. Schmidt, (Miss) C. M. S. Savoy, and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1943, 65, 296—297).—*p*-C<sub>6</sub>H<sub>4</sub>Ph·OAc and Cl<sub>2</sub> in AcOH give the 4'-Cl-derivative (cf. A., 1943, II, 28).

R. S. C.

**Equilibrium between borate ion, pyrocatechol, and pyrocatechol borate ion in aqueous solution, and the preparation of monopyrocatechol borates.**—See A., 1943, I, 160.

**Synthesis of polyenes. III. Synthesis of diethylstilboestrol.** M. S. Kharasch and M. Kleiman (*J. Amer. Chem. Soc.*, 1943, 65, 11—15; cf. A., 1940, II, 362).—Adding NaNH<sub>2</sub> to CHPhMeCl (prep. from CHPh·CH<sub>2</sub> by dry HCl at -80°; 68% yield, b.p. 73°/11 mm., in liquid NH<sub>3</sub> gives CHPhMe·CPhMeCl, b.p. 147—148°/11 mm., which when repeatedly distilled in vac., gives HCl and *trans*-(CPhMe)<sub>2</sub>; the reverse addition gives 40% of *cis*-(CPhMe)<sub>2</sub> and high-boiling oils. Adding CHPhEtCl (0.1) (prep. from CHPhEt·OH by dry HCl at 0°; 55% yield), b.p. 85—87°/15 mm., in PhMe to NaNH<sub>2</sub> (0.3 mol.) in liquid NH<sub>3</sub> gives a mixture, b.p. (mostly) 162—164°/12 mm., of CHPhEt·CPhEtCl + (?) (CPhEt)<sub>2</sub>, which with H<sub>2</sub>-Pt-black-EtOH or Na-NH<sub>3</sub> gives (CHPhEt)<sub>2</sub>, m.p. 88.5—89°, and with Br-CCl<sub>4</sub> gives a dibromide, C<sub>18</sub>H<sub>20</sub>Br<sub>2</sub> [?(CPhEtBr)<sub>2</sub>], m.p. 166.5°. Adding *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>EtBr (I) [prep. from anethole (II)-PhMe by dry HBr at -80°] in PhMe to an excess of NaNH<sub>2</sub> in NH<sub>3</sub> gives a substance (γδ-di-*p*-anisyl-Δ<sup>n</sup>-hexene or 1 : 2-di-*p*-anisyl-3-methyl-1-ethylcyclopropane) (III) (34—40%), m.p. 120.5°, and high-boiling products, including a hexameride, m.p. 209—210°, of (II). (III) depresses the m.p. of *trans*-(*p*-OMe·C<sub>6</sub>H<sub>4</sub>·CET)<sub>2</sub> (IV), m.p. 124°, absorbs 1 H<sub>2</sub> (Pt-black; MeOH) to give (*p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>Et)<sub>2</sub> (V), m.p. 142°, and with KOH in (CH<sub>2</sub>·OH)<sub>2</sub> (vac.) at 224° gives (*p*-OH·C<sub>6</sub>H<sub>4</sub>·CET)<sub>2</sub> (55.5% if the residual oil is re-treated), m.p. 165—166°, identified by mixed m.p., as diacetate and dibenzoate, and by its absorption spectrum. Non-identity of (III) and (IV) and identity of (V) with an authentic specimen are confirmed by crystallo-optical data. Adding (I) (2 mols.) and then Na (1 atom) to NaNH<sub>2</sub> (1 mol.) in NH<sub>3</sub> gives 80% of *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>Et·NH<sub>2</sub> [hydrochloride, m.p. 215° (decomp.); Bz derivative, m.p. 120°].

R. S. C.

**Structures of 4 : 4'-dihydroxy- [and 4 : 4'-dimethoxy-]αβ-diethylstilbene.**—See A., 1943, I, 118.

**Auroxanthin, a carotene pigment which absorbs light of short wave-length.** P. Karrer and J. Rutschmann (*Helv. Chim. Acta*, 1942, 25, 1624—1627; cf. Kuhn *et al.*, A., 1931, 491).—In addition to violaxanthin (I) the mixture of carotenoids from *Viola tricolor* contains flavoxanthin and auroxanthin, C<sub>40</sub>H<sub>60</sub>(<sub>62</sub>)O<sub>5</sub>, m.p. 191—192° (vac.). The absorption spectrum of auroxanthin lies more in the region of short λ than does that of any other carotenoid, whence it follows that it has only 8 conjugated double linkings. Microhydrogenation indicates the presence of 8 or 9 double linkings. The colour reactions of auroxanthin and violaxanthin with HCl are very closely similar. Of the 5 O, 4 and probably all are present as OH; CO is absent.

H. W.

**Attempted asymmetric syntheses employing choleic acids.** C. C. Reid and J. M. Sturtevant (*J. Amer. Chem. Soc.*, 1943, 65, 125).—Bromination of the crotonic-choleic acid complex and prep. of CHPhMe·OH from CPhMe by hydrogenation in aq. Na deoxycholate give inactive products. The complex, ICPhMe + 3deoxycholic acid (I), m.p. 167—168° (corr.), could not be reduced [catalyst or Al(OPr<sup>i</sup>)<sub>3</sub>-C<sub>6</sub>H<sub>6</sub>]. CHPhMe·OH could not be obtained from the complex, PhCHO + 2(I), m.p. 164—165°, by MgMeBr.

R. S. C.

**Vinyl alcohols. IV. Oxidative cleavage.** R. C. Fuson, D. J. Byers, A. I. Rachlin, and P. L. Southwick. **V. Isomeric bromo-αβ-dimesityl-Δ<sup>n</sup>-propen-α-ols.** R. C. Fuson, R. V. Lindsey, jun., and P. B. Welldon (*J. Amer. Chem. Soc.*, 1942, 64, 2886—2888, 2888—2891; cf. A., 1942, II, 92).—IV. Mes·CMe·CMe·OH (Mes = mesityl) is stable in absence of air but in air gives MesCO<sub>2</sub>H, MesOH, and CO, with small amounts of MesCO<sub>2</sub>H (I), CH<sub>2</sub>·CMe·COMes, H<sub>2</sub>, and a phenol, C<sub>18</sub>H<sub>22</sub>O<sub>2</sub>, m.p. 169.5—171.5° (diacetate, m.p. 148—149°). 2 : 3 : 5 : 6 : 1-C<sub>6</sub>HMe<sub>4</sub>·C(OH)·CMeMes with O<sub>2</sub> in COMe<sub>2</sub> gives similarly MesCO<sub>2</sub>H, durenol, and CO with small amounts of 2 : 3 : 5 : 6 : 1-C<sub>6</sub>HMe<sub>4</sub>·CO<sub>2</sub>H, 2 : 3 : 5 : 6 : 1-C<sub>6</sub>HMe<sub>4</sub>·CO·CMe·CH<sub>2</sub>, and H<sub>2</sub>.

V. (I) and Br (no Fe) give 2 : 4 : 6 : 3 : 1-C<sub>6</sub>HMe<sub>3</sub>Br·CO<sub>2</sub>H (74%), m.p. 162—165°, the chloride (prep. by SOCl<sub>2</sub>), b.p. 175—178°/28 mm., of which with CH<sub>2</sub>Mes·MgCl in Et<sub>2</sub>O at 0° gives 3'-bromodeoxymesitoin (II) (45%), m.p. 91—92° [or sometimes mainly (CH<sub>2</sub>Mes)<sub>2</sub>]. CH<sub>2</sub>Mes·COCl, 1 : 3 : 5 : 2-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>Br (III), and AlCl<sub>3</sub> in CS<sub>2</sub> at 0—17° give, by migration of Br, 3-bromodeoxymesitoin (IV) (90%), m.p. 98—99°. Condensation of (II) and (IV) with CH<sub>2</sub>O yields 3-bromomesityl α-mesitylvinyl (V), m.p. 150—151°, and mesityl α-3-bromomesitylvinyl ketone (VI), m.p. 149—150° [mixed with (V), 131—134°], respectively. H<sub>2</sub>-PtO<sub>2</sub> in AcOH reduces (V) and (VI) to unstable solid propenols; that from (V) with Na followed by Me<sub>2</sub>SO<sub>4</sub> in hot C<sub>6</sub>H<sub>6</sub> gives α-methoxy-α-3-bromomesityl-β-mesityl-Δ<sup>n</sup>-propene, m.p. 117.5—119°, and with O<sub>2</sub> in COMe<sub>2</sub> gives MesCO<sub>2</sub>H and 2 : 4 : 6 : 3 : 1-C<sub>6</sub>HMe<sub>3</sub>Br·OH; that from (VI) with O<sub>2</sub> gives 2 : 4 : 6 : 3 : 1-C<sub>6</sub>HMe<sub>3</sub>Br·COMe and MesOH. (II) is unchanged by AlCl<sub>3</sub> in CS<sub>2</sub>, (CH<sub>2</sub>O)<sub>3</sub>, (III), ZnCl<sub>2</sub>, and conc. HCl at 65—70° give 3-bromomesitylmethyl chloride, m.p. 44—45°, b.p. 126—129°/2 mm., converted by NaCN in aq. EtOH at 55—60° into 3-bromomesityl-acetonitrile, m.p. 113—114°; hydrolysis (boiling 55% H<sub>2</sub>SO<sub>4</sub>) to the acid, m.p. 168.5—169.5° (some amide, m.p. 231—232°, also obtained), conversion thereof into the chloride, b.p. 146—148°/4 mm., by SOCl<sub>2</sub>, and Friedel-Crafts reaction with s-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub> gives (IV).

R. S. C.

**5-Amino-2-methoxybenzyl alcohol.**—See B., 1943, II, 145.

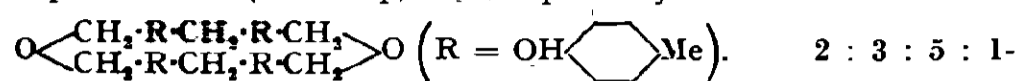
**Phenol-formaldehyde resins. III. Condensation with dihydroxybenzenes and dihydroxybenzene alcohols : a principle of Bakelite production from wood-tar phenols.** H. von Euler, E. Adler, S. de Kispéczy, and A. M. Fagerlund (*Arkiv Kemi, Min., Geol.*, 1941, 14, A, No. 10, 20 pp.).—o-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> and 40% CH<sub>2</sub>O in 10% aq. NaOH and N<sub>2</sub> at room temp. for 2 days, followed by Me<sub>2</sub>SO<sub>4</sub>-aq. NaOH, afford 1 : 2 : 3 : 6-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>·OH)<sub>2</sub>, m.p. 92°, oxidised by KMnO<sub>4</sub>-aq. NaOH, to 2 : 3-dimethoxyterephthalic acid, m.p. 206—208° (sinters at 195°) [48% HBr then gives the 2 : 3-(OH)<sub>2</sub>-acid, new m.p. 293—293.5° (decomp.)]. 1 : 4 : 2 : 3 : 5 : 6-(OH)<sub>2</sub>C<sub>6</sub>(CH<sub>2</sub>·OH)<sub>4</sub> and *m*-4-xylene (I) or *p*-cresol in boiling EtOH-conc. HCl give 2 : 3 : 5 : 6-tetra-(2'-hydroxy-3' : 5'-dimethylbenzyl)-quinol, m.p. 271—272° (C<sub>5</sub>H<sub>5</sub>N compound, m.p. 89°; hexa-acetate, m.p. 275.5—276.5°), or 2 : 3 : 5 : 6-tetra-(2'-hydroxy-5'-methylbenzyl)-quinol, m.p. 265—267° (hexa-acetate, m.p. 222—222.5°), respectively. (I) and CH<sub>2</sub>O-aq. NaOH give 4 : 1 : 3 : 5-OH·C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·CH<sub>2</sub>·OH (II), m.p. 56—57°, which with quinol-EtOH-HCl yields CH<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·OH-1 : 3 : 5 : 2)<sub>2</sub> and 2 : 5-di-(2'-hydroxy-3' : 5'-dimethylbenzyl)quinol, m.p. 293—296° (tetra-acetate, m.p. 212.5—213°); the latter is also obtained from 1 : 4 : 2 : 5-(OH)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>·OH)<sub>2</sub> and (I) in EtOH-HCl. (II) and o-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>-HCl-EtOH give a di-(2'-hydroxy-3' : 5'-dimethylbenzyl)pyrocatechol, m.p. 190.5° (tetra-acetate, m.p. 147°), different from the 3 : 6-disubstituted isomeride, m.p. 227°, obtained from 1 : 2 : 3 : 6-(OH)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>·OH)<sub>2</sub> and (I). (II) and *m*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> yield 2 (or 6)-2'-hydroxy-3' : 5'-dimethylbenzylresorcinol, m.p. 226—227°. Resols are formed during condensation (alkali) of a mixture of a bifunctional phenol and o- or *p*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> with CH<sub>2</sub>O; these can be hardened by heat. Such a condensation can be applied to the mixed phenols from wood tar.

A. T. P.

**Phenol-formaldehyde resins. IV. Mechanism of hardening of resols. Hardening of di-*p*-tolylmethane monoalcohol.** E. Adler. **V. Constitution of hardening product of di-*p*-tolylmethane monoalcohol.** E. Adler, H. von Euler, and H. G. Hasselquist. **VI. Hardening of di-*p*-tolylmethane dialcohol.** VII. Cyclic ether from di-*p*-tolylmethane dialcohol. H. von Euler, E. Adler, and B. Bergström (*Arkiv Kemi, Min., Geol.*, 1941, 14, A, No. 23, 7 pp.; No. 24, 8 pp.; No. 25, 6 pp.; No. 30, 6 pp.).—IV. (2 : 5 : 1-OH·C<sub>6</sub>H<sub>3</sub>Me)<sub>2</sub>CH<sub>2</sub> and CH<sub>2</sub>O-aq. NaOH give 2-hydroxy-3-(2'-hydroxy-5'-methylbenzyl)-5-methylbenzyl alcohol (I), m.p. 136—136.5°, and some 2 : 2'-dihydroxy-5 : 5-dimethyl-3 : 3'-di(hydroxymethyl)diphenylmethane (II), m.p. 151—151.5°, also obtained from (I) and CH<sub>2</sub>O-aq. NaOH. Elimination of 1 mol. of H<sub>2</sub>O from 2 mols. of (I) during hardening at 125—127° affords di-[2-hydroxy-3-(2'-hydroxy-5'-methylbenzyl)-5-methylbenzyl] ether (III), m.p. 179—179.5°. V. The constitution of (III) is discussed and confirmed. (III) affords a tetrabenzoate, m.p. 173—175°, and a tetra-*p*-nitrobenzoate, m.p. 255°. (I) and HBr-C<sub>6</sub>H<sub>14</sub> give 2-hydroxy-3-(2'-hydroxy-5'-methylbenzyl)-5-methylbenzyl bromide (IV), dimorphic, m.p. 139.5—140°, also obtained similarly from (III). (IV) is converted by AcOH-NaOAc into the -benzyl acetate, m.p. 109.5—110°. Di-(3-bromo-4-methoxy-2 : 5-dimethylbenzyl) ether, m.p. 71—72°, is prepared from the 4 : 4'-(OH)<sub>2</sub>-compound and Me<sub>2</sub>SO<sub>4</sub>-aq. NaOH.

VI. (II) at 150° (30 min.) loses 0.9—1 mol. of H<sub>2</sub>O and ~0.2 mol. of CH<sub>2</sub>O, giving a cryst. compound (V) and resin (A). (A) or (V) with HBr-CHCl<sub>3</sub> at -20° affords 2 : 2'-dihydroxy-3 : 5'-dimethyl-3 : 3'-di(bromomethyl)diphenylmethane (VI), m.p. 151° (decomp.), also obtained from (II) and HBr-EtOH at -20°.

VII. (V) gives (CH<sub>2</sub>N<sub>2</sub>) a Me<sub>4</sub> ether, m.p. 260—262° (immersed at 250°), a tetra-acetate, m.p. 306° (decomp.), and when heated affords an amorphous product, m.p. >360°. At 250°, (V) eliminates 0.26 mol. of CH<sub>2</sub>O and ~3 mols. of H<sub>2</sub>O and yields a product, m.p. 123—125° (not sharp). (V) is probably



OH-C<sub>6</sub>H<sub>4</sub>-Me<sub>2</sub>-CH<sub>2</sub>-OH at 140° probably gives 4 : 6-dimethyl-2-hydroxymethylphenyl 2-hydroxy-3 : 5-dimethylbenzyl ether.

A. T. P.

Phenol-formaldehyde resins. XI. Mechanism of the hardening of resols. Formation of dihydroxydibenzyl ethers. H. von Euler, E. Adler, G. Eklund, and O. Törngren (*Arkiv Kemi, Min., Geol.*, 1942, 15, B, No. 9, 8 pp.).—Very gradual addition of 40% CH<sub>2</sub>O to an aq. solution of *p*-cresol and NaOH gives 2 : 5 : 1-OH-C<sub>6</sub>H<sub>4</sub>-Me-CH<sub>2</sub>-OH, m.p. 106—107°, converted at 150° for 30 min. in a sealed tube into di-2-hydroxy-5-methylbenzyl ether (I), m.p. 101—102°, in 10% yield; it gives an unstable, pale violet colour with FeCl<sub>3</sub>-EtOH. (I) is transformed by HBr in CHCl<sub>3</sub> at 0° into the very unstable bromide, which can be converted by immediate treatment with aq. NaHCO<sub>3</sub> into the (? trimeric) quinonemethide, m.p. 150—151°, which is insol. in alkali and does not give a colour with FeCl<sub>3</sub>. 2 : 3 : 5 : 1-OH-C<sub>6</sub>H<sub>4</sub>-Me<sub>2</sub>-CH<sub>2</sub>-OH (II) is transformed by NaOH and *p*-C<sub>6</sub>H<sub>4</sub>-Me-SO<sub>2</sub>Cl into 2 : 4-dimethyl-6-hydroxymethylphenyl *p*-toluenesulphonate, m.p. 59—60°, which requires a temp. of 200° for conversion into the corresponding ether di-*p*-toluenesulphonate, m.p. 105—106°, hydrolysed to (2 : 3 : 5 : 1-OH-C<sub>6</sub>H<sub>4</sub>-Me-CH<sub>2</sub>)<sub>2</sub>O, m.p. 99—100°. (II) and *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-COCl (Schotten-Baumann) afford 2 : 4-dimethyl-6-hydroxymethylphenyl *p*-nitrobenzoate, m.p. 122°, but mainly the di-*p*-nitrobenzoate, m.p. 166—167°.

H. W.

Phenol-formaldehyde resins. XII. Mechanism of the hardening of resols. Hardening of 3-bromo-2-hydroxy-5-methylbenzyl alcohol. E. Adler, S. Tingstam, and O. Caspersson (*Arkiv Kemi, Min., Geol.*, 1942, 15, B, No. 10, 8 pp.).—4 : 2 : 1-C<sub>6</sub>H<sub>4</sub>-MeBr-OH is slowly converted by NaOH and CH<sub>2</sub>O at room temp. into 3-bromo-2-hydroxy-5-methylbenzyl alcohol (I), m.p. 35—36°, which gives a pure blue colour with FeCl<sub>3</sub> in EtOH. (I) at 150° (sealed tube) for 2 hr. gives a little CH<sub>2</sub>O, (mainly) di-3-bromo-2-hydroxy-5-methylbenzyl ether, m.p. 75.5—76.5° (Me<sub>2</sub> ether, m.p. 86—87°), which gives a violet colour with FeCl<sub>3</sub>, and a small proportion of the (probably trimeric) quinonemethide (II), (C<sub>6</sub>H<sub>4</sub>OBr)<sub>3</sub>, m.p. 259°. (I) differs from 2 : 3 : 5 : 1-OH-C<sub>6</sub>H<sub>4</sub>-Me<sub>2</sub>-CH<sub>2</sub>-OH (III) in that it does not yield a diphenylmethane derivative under these conditions. At 180° (III) gives mainly the corresponding trimeric quinonemethide as main component of the crystallisable material whereas (I) gives little (II) and mainly αβ-di-3-bromo-2-hydroxy-5-methylphenylethane, m.p. 148—149°. (I) and HBr in well-cooled CHCl<sub>3</sub> afford 3-bromo-2-hydroxy-5-methylbenzyl bromide, m.p. 51—51.5°, which gives (II), m.p. 262—262.5°, when dissolved in Et<sub>2</sub>O and shaken with 2N-Na<sub>2</sub>CO<sub>3</sub>.

H. W.

Arylacetonitrile derivatives.—See B., 1943, II, 145.

Derivatives of aminobenzamides.—See A., 1943, II, 175.

Antispasmodics. I. Basic esters of arylacetic acids. R. R. Burtner and J. W. Cusic (*J. Amer. Chem. Soc.*, 1943, 65, 262—267).—Fluorene with LiBu<sup>a</sup> (prep. described) in boiling Et<sub>2</sub>O or NaPh (prep. described) in C<sub>6</sub>H<sub>6</sub>-N<sub>2</sub> (later adding Et<sub>2</sub>O) and pouring on to solid CO<sub>2</sub> gives fluorene-9-carboxylic acid. Diphenylacetylhydrazide hydrochloride, m.p. 298°, with NaNO<sub>2</sub>-H<sub>2</sub>O-PhMe at 5° and then NEt<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>-OH (I) at 100° gives β-diethylaminoethyl diphenylmethylcarbamate [hydrochloride, m.p. 184—185° (lit. 179°)]. α- or β-Naphthyl with KOEt-EtOH-Et<sub>2</sub>O at room temp. gives 1-, m.p. 133—134° (decomp.) (lit. 137°), or 2-naphthilic acid, m.p. 175° (decomp.) (scarlet colour in conc. H<sub>2</sub>SO<sub>4</sub>), respectively, reduced by HI-aq. AcOH to di-α-, m.p. 224° (lit. 223°), or di-β-naphthylacetic acid, m.p. 190°, respectively. CN-CPh<sub>2</sub>-CO<sub>2</sub>Me with H<sub>2</sub>-Raney Ni in EtOH at room temp./45 lb. gives Me β-amino-αα-diphenylpropionate hydrochloride, m.p. 202° (decomp.) (derived acid, m.p. 360°), converted by NaNO<sub>2</sub>-HCl-H<sub>2</sub>O at 0° into Me β-hydroxy-αα-diphenylpropionate, m.p. 103° (derived acid, m.p. 167—168°). 2-Nitrofluorene-9-carboxylic acid with, successively, PCl<sub>5</sub> at 100°, (I)-C<sub>6</sub>H<sub>5</sub> at room temp., and Raney Ni-H<sub>2</sub>-EtOH-C<sub>6</sub>H<sub>6</sub> gives β-diethylaminoethyl 2-aminofluorene-9-carboxylate hydrochloride, m.p. 92—94° (decomp.). Anthracene-9-carboxylic acid is best obtained from the aldehyde by Ag<sub>2</sub>O-NaOH-H<sub>2</sub>O-EtOH. 9-Formylfluorene, CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub>, and piperidine at 85° give γ-2 : 2-diphenylenecrotonic acid, m.p. 202—203°. (CHPh-OH)<sub>2</sub> (prep. from benzoin by Raney Ni-H<sub>2</sub> in dioxan; not SnCl<sub>4</sub>-EtOH) and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> give CHPh<sub>2</sub>·CHO, which with CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> and piperidine at 85° gives γγ-diphenylcrotonic acid (73%), m.p. 115—116°. Et tropate and thence the acid are best prepared from CHO-CHPh-CO<sub>2</sub>Et by Raney Ni-H<sub>2</sub>-

EtOH. The following ester hydrochlorides are prepared from the alcohol and acid chloride or dialkylaminoalkyl chloride and acid in, e.g., Pr<sup>o</sup>OH : NEt<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>, tropine (sulphate), and NEt<sub>2</sub>·CMe<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>, tropate (phosphate); NEt<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>, m.p. 98—99°, and 4-hydroxy-1-methylpiperidine atropate; NEt<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub> α-phenyltropate, m.p. 143—144°, diphenylacetate, m.p. 112°, benzilate, m.p. 177—178°, β-hydroxy-β-phenylpropionate, m.p. 141—142°, anisilate, m.p. 172°, α-chloro-diphenylacetate, m.p. 149—151°, ββ-diphenylacrylate, m.p. 159—160°, γγ-diphenylcrotonate, hygroscopic, m.p. 114—118°, fluorene-9-carboxylate (II), m.p. 143—144°, 9-hydroxyfluorene-9-carboxylate, m.p. 204°, 9-fluorenylacetate, m.p. 130—132°, γ-2 : 2-diphenylenecrotonate, m.p. 205°, di-α-, m.p. 211°, and -β-naphthylacetate, m.p. 151°, 1-, m.p. 143—144°, and 2-naphthilate, m.p. 195°, α-phenyl-β-2-furylacrylate, m.p. 157°, anthracene-9-carboxylate, m.p. 162°, and hydrindene-2-carboxylate, m.p. 132—133°; (NEt<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>)<sub>2</sub> dl-camphorate, hygroscopic; NMe<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>, m.p. 164°, 4-hydroxy-1-methyl-, hygroscopic, -1-n-butyl-, m.p. 162°, -1-β-phenylethyl-, m.p. 218—219°, and -1 : 2 : 6-trimethyl-piperidine diphenylacetate, hygroscopic; NEt<sub>2</sub>·[CH<sub>2</sub>]<sub>3</sub>, m.p. 220°, NEt<sub>2</sub>·CHMe·CH<sub>2</sub>, m.p. 177°, NBU<sup>a</sup>·[CH<sub>2</sub>]<sub>2</sub>, m.p. 165°, NHBu<sup>β</sup>·[CH<sub>2</sub>]<sub>2</sub>, m.p. 160°, 4-hydroxy-1-methyl-, m.p. 218°, -1-β-phenylethyl-, m.p. 157—158°, and -1 : 2 : 6-trimethyl-piperidine fluorene-9-carboxylate, m.p. 217—218°. Diphenylacet-, m.p. 145°, and fluorene-9-carboxyl-, a syrup, -β-diethylaminoethylamide hydrochloride are also prepared. Of these esters and amides, (II) has the most favourable therapeutic index as an antispasmodic. R. S. C.

Optically active nitro- and amino-mandelic acids. I. A. Fredga and E. Andersson (*Arkiv Kemi, Min., Geol.*, 1941, 14, B, No. 18, 7 pp.).—*r-m*-Nitromandelic acid (I) is resolved into (-)-, m.p. 133—134°, [α]<sub>D</sub><sup>25</sup> -122.4° in H<sub>2</sub>O (brucine salt, +0.5H<sub>2</sub>O, decomp. 148—150°), and (+)-*m*-nitromandelic acid, m.p. 133—134°, [α]<sub>D</sub><sup>25</sup> +122.6° in H<sub>2</sub>O (cinchonine salt, +0.5H<sub>2</sub>O or anhyd.). Reduction by aq. FeSO<sub>4</sub>-Ba(OH)<sub>2</sub> affords (-)- (+H<sub>2</sub>O) (II), m.p. 128—128.5° (decomp. >129°), [α]<sub>D</sub><sup>25</sup> -98.1° in H<sub>2</sub>O (also by H<sub>2</sub>-Pd-C-H<sub>2</sub>O), and (+)-*m*-aminomandelic acid, m.p. 128—128.5° (decomp. >129°), [α]<sub>D</sub><sup>25</sup> +98.2° in H<sub>2</sub>O, respectively. (I) is reduced H<sub>2</sub>-Pd-H<sub>2</sub>O to *r-m*-aminomandelic acid, m.p. 130°, converted by the diazo-reaction (aq. NaH<sub>2</sub>PO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-CuSO<sub>4</sub>) into *r*-mandelic acid, m.p. 117—118°; (II) similarly gives (-)-mandelic acid, m.p. 131.5—132.5°, [α]<sub>D</sub><sup>25</sup> -152° in H<sub>2</sub>O. A. T. P.

Optical activity of nitro- and amino-mandelic acids. E. Grimsell (Andersson) (*Arkiv Kemi, Min., Geol.*, 1942, 15, B, No. 17, 11 pp.).—Conductivity data are given for *o*-, *m*-, and *p*-nitromandelic acid and their *K* salts (cf. McKenzie *et al.*, A., 1935, 356), and optical data for *l*(+)-mandelic acid, its *o*-, *m*-, and *p*-NO<sub>2</sub>- and -NH<sub>2</sub>-derivatives in various solvents. *r-o*-Nitromandelic acid is reduced (Na salt-H<sub>2</sub>O-H<sub>2</sub>-Pd-C) to *r-o*-aminomandelic acid, m.p. 144°, deaminated to mandelic acid. (-)-*o*-Aminomandelic acid similarly gives (-)-mandelic acid. A. T. P.

Synthesis of cinnamic acids from methyl acrylate or acrylonitrile and diazonium salts. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, 65, 57—58).—Adding aq. ArN<sub>2</sub>Cl to CH<sub>2</sub>·CH·CN-NaOAc-CuCl<sub>2</sub>-COMe<sub>2</sub> (pH ~6) gives 34—48% of α-chloro-β-phenyl-, m.p. 18—21°, b.p. 137—140°/15 mm., α-chloro-β-*m*- (impure), m.p. 83—84°, b.p. 215—225°/13 mm., and -*p*-nitrophenyl-, m.p. 111—112°, and α-chloro-β-*p*-tolyl-, b.p. 140—145°/11 mm., -propionitrile, converted in boiling NPhEt<sub>2</sub> into CHAr·CH·CN. CH<sub>2</sub>·CH·CO<sub>2</sub>Me reacts similarly but gives rather poorer yields. *p*-Nitrocinnamionitrile, m.p. 200—201°, and impure Me α-chloro-β-*p*-tolylpropionate, b.p. 135—145°/11 mm., are described. R. S. C.

Condensation of malonanilic acid with aldehydes. V. With *o*- and *p*-chlorobenzaldehydes and *m*-bromobenzaldehyde; influence of the halogens. K. C. Pandya and (Miss) R. B. Pandya (*Proc. Indian Acad. Sci.*, 1943, 17, A, 1—6).—NHPh·CO·CH<sub>2</sub>·CO<sub>2</sub>H with RCHO gives CHR·C(CO<sub>2</sub>H)·CO·NHPh with a little CHR·CH·CO·NHPh (I). In presence of C<sub>6</sub>H<sub>5</sub>N, (I) is predominant. The following were prepared: *p*-chloro-, m.p. 190°, *o*-chloro-, m.p. 225°, and *m*-bromobenzylidenemalonanilic acid, m.p. 186—188°; *p*-chloro-, m.p. 180°, *o*-chloro-, forms, m.p. 176—177° and 153—154°, and *m*-bromo-cinnam-anilide, forms, m.p. 128—129° and (probably) 162°. F. R. G.

Fatty derivatives of salicylic acid and α-naphthol. D. Price and (Miss) E. L. May (*J. Amer. Chem. Soc.*, 1943, 65, 297).—*o*-OH-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>Me and *n*-C<sub>10</sub>H<sub>19</sub>-COCl at 220—225° give Me *o*-decoyl-oxybenzoate, b.p. 217—219°/12 mm., converted (Fries; light petroleum) into Me 4(?)5-decoylsalicylate, m.p. 66.5—67.5°, b.p. 180—190°/1.5 mm. (derived acid, m.p. 120.5—121.5°). α-C<sub>10</sub>H<sub>7</sub>*n*-octoate, b.p. 156—157°/1 mm., and 2-octoyl-1-naphthol, m.p. 68—68.5°, are also prepared. R. S. C.

Sulphonyl derivatives of amidines and imino-ethers. H. J. Barber (*J.C.S.*, 1943, 101—104).—*p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>Cl (I) (prep. described), b.p. 143—144°/1.5 mm., with NH·CPh·OEt (2 mols.) (II) in COMe<sub>2</sub> at 30—35° affords *p*-nitrobenzenesulphonylbenzimidino Et ether (III), m.p. 129—130°, or with NH·CPh·NH<sub>2</sub>·HCl in aq. NaOH-COMe<sub>2</sub> gives *N-p*-nitrobenzenesulphonylbenzimidine (IV), m.p. 179° (decomp.). (III) and NH<sub>3</sub>-EtOH give an isomeride, m.p. 159—165° (previous softening) (decomp. ~195—200°), of (IV), converted by prolonged boiling in EtOH into (IV). (IV) loses SO<sub>2</sub> at 200° to

give *p*-nitrophenylbenzamidine, m.p. 167—168°. (II) (as hydrochloride) and *p*-NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Cl (V)—C<sub>5</sub>H<sub>5</sub>N at 70° yield *p*-acetamidobenzenesulphonylbenzimidino Et ether, m.p. 100—102°, converted at 110—120° into a form, m.p. 136—137°. Either form with NH<sub>3</sub>—EtOH yields *p*-acetamidobenzenesulphonylbenzamidine,  $\alpha$ -, m.p. 185—187° (pre-heated), or  $\beta$ -form, m.p. 208—210° [formed by more prolonged action of EtOH—NH<sub>3</sub>; also obtained from (V) and NH<sub>3</sub>·CPh·NH<sub>2</sub>]. Hydrogenation (PtO<sub>2</sub>, 2 atm.) of (III) in COMe<sub>2</sub> at room temp. gives *p*-aminobenzenesulphonylbenzimidino Et ether, m.p. 98°, converted by NH<sub>3</sub>—EtOH into the corresponding benzamidine,  $\alpha$ -, m.p. 155—160°, or  $\beta$ -form, m.p. 205—207°. NH<sub>3</sub>·CMe·OEt and (I) in Et<sub>2</sub>O at ~25° give *p*-nitrobenzenesulphonylacetimino Et ether, m.p. 87—88°; in 1 case (in boiling Et<sub>2</sub>O) *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NHAc was the main product. *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>Na and NPh<sub>2</sub>·CPhCl heated gradually to 180° yield BzCl and NN'-diphenylbenzamidine *p*-nitrobenzenesulphonate, m.p. 240—241°, converted by cold aq. NaOH into NPh<sub>2</sub>·CPh·NHPh. N-*p*-Nitrobenzenesulphonylbenzimidino Ph ether, m.p. 173—174° (decomp. 280—285°, with some evolution of SO<sub>2</sub>), is obtained from *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·N·CPhCl, new m.p. 164—165°, and PhOH—NaOH (10:1) at 40°, then at 100°. (I) and *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NNaPh at 150—200° give di-*p*-nitrobenzenesulphonylanilide, m.p. 264°. A. T. P.

**$\beta$ -Cyano- $\beta$ -phenylpropionic acid.** S. Wideqvist (*Arkiv Kemi, Min., Geol.*, 1941, 14, B, No. 19, 6 pp.).—CHPh·C(CO<sub>2</sub>Et)<sub>2</sub> and KCN—aq. EtOH give CN·CHPh·CH<sub>2</sub>·CO<sub>2</sub>H, m.p. 75° (lit. 150°), converted by conc. HCl at 115° into CO<sub>2</sub>H·CHPh·CH<sub>2</sub>·CO<sub>2</sub>H, or by conc. H<sub>2</sub>SO<sub>4</sub> at room temp. (12 hr.) or H<sub>2</sub>O at 25° (10 days) into CO<sub>2</sub>H·CH<sub>2</sub>·CHPh·CO·NH<sub>2</sub>. A. T. P.

**Urethanes. VII. Reactions of acyl diurethanes with ammonia and primary amines.** Stabilising effect of the phenyl radical in phenylmalonyl- and phenylsuccinyl-diurethane. S. Basterfield and A. J. Dyck (*Canad. J. Res.*, 1942, 20, B, 240—245).—Introduction of Ph increases the stability of the mol. CHPh(CO·NH·CO<sub>2</sub>Et)<sub>2</sub> (I) and 25% aq. NH<sub>3</sub> at room temp. slowly give CHPh(CO·NH<sub>2</sub>)<sub>2</sub>, m.p. 232°, NH<sub>2</sub>·CO<sub>2</sub>Et (II), and some (?) NH<sub>4</sub> phenylbarbiturate. Under similar conditions (I) and 25% NH<sub>2</sub>Et afford phenylmalonethylamide, m.p. 154°, (II), and, probably, NH<sub>3</sub>Et phenylbarbiturate. With NH<sub>2</sub>Ph and (I) at 150° the products are phenylmalonanilide (III), m.p. 204—205°, phenylmalonyldiphenylcarbamide, m.p. 234—235° [converted by NH<sub>2</sub>Ph at 150—160° into (III) and CO(NHPh)<sub>2</sub>], and phenylcarbamidophenylmalonylurethane, m.p. 151°; at 180—190° (III) and CO(NHPh)<sub>2</sub> are produced. CO<sub>2</sub>H·CH<sub>2</sub>·CHPh·CO<sub>2</sub>H, (II), and POCl<sub>3</sub> at room temp., then at 40°, and finally at 50° afford phenylsuccinyl-diurethane (IV), m.p. 162°, slowly transformed by 25% NH<sub>3</sub> at room temp. into NH<sub>2</sub>·CO·CHPh·CH<sub>2</sub>·CO·NH<sub>2</sub> and (II). Similarly NH<sub>2</sub>Et gives phenylsuccinethylamide, m.p. 179—180°, and (II). With NH<sub>2</sub>Ph at 180° the main product is (?) phenylsuccinyl-diphenylcarbamide (V), m.p. 235°, with CO(NHPh)<sub>2</sub> and a gum, whereas at 180—200° (V), (?) phenylcarbamidophenylsuccinanilide, m.p. 234°, and CO(NHPh)<sub>2</sub> result. Malonyldiurethane and cyclohexylamine rapidly give malonocyclohexylamide, m.p. 174°, and (II). H. W.

**$\beta$ -Arylglutaconic acids. VII. Constitution of the so-called hydroxy-anhydrides.** G. R. Gogte (*Proc. Indian Acad. Sci.*, 1942, 16, A, 240—243).—Earlier work on  $\alpha$ -acyl- and  $\alpha$ -diacyl- $\beta$ -arylglutaconic anhydrides (cf. A., 1938, II, 284; 1939, II, 133; 1941, II, 103) is reviewed. Contrary to Limaye *et al.* (A., 1940, II, 130), no  $\alpha$ -Me derivative is obtained from *p*-OMe·C<sub>6</sub>H<sub>4</sub>·C(CH<sub>2</sub>CO<sub>2</sub>Et)·CH<sub>2</sub>·CO<sub>2</sub>Et by NaOEt—MeI. Reduction or attempted esterification of *p*-OMe·C<sub>6</sub>H<sub>4</sub>·C(CH<sub>2</sub>CO<sub>2</sub>H)·CHAc·CO<sub>2</sub>Et gives only the lactone,  $\text{CAr} \begin{array}{c} \text{CH} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{CO}_2\text{Et}) \text{---} \text{CMe} \end{array} \text{O}$ . Decomp. occurs before CO<sub>2</sub>Et·CH<sub>2</sub>·CO·CHMe·CO<sub>2</sub>Et can be condensed with ArOAlk by H<sub>2</sub>SO<sub>4</sub>. R. S. C.

**Preparation of aldehydes from carboxylic acids with titanium dioxide as catalyst.**—See A., 1943, II, 152.

**Condensation of chlorodinitrotoluenes with *p*-nitrosodimethylaniline.** D. S. Mittal (*J. Indian Chem. Soc.*, 1942, 19, 408).—The requisite C<sub>6</sub>H<sub>2</sub>MeCl(NO<sub>2</sub>)<sub>2</sub> with *p*-NO·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub> in presence of EtOH and Na<sub>2</sub>CO<sub>3</sub> and hydrolysis of the resulting products with 2N-HNO<sub>3</sub> leads to 5-chloro-2:4-dinitro-, m.p. 150—152° (phenylhydrazone, m.p. 217°; oxime, m.p. >280°), 4-chloro-3:5-dinitro-, m.p. 79—80° (phenylhydrazone, m.p. 109°; anil, m.p. 108°; oxime, m.p. >290°); and 2-chloro-3:5-dinitro-benzaldehyde, m.p. 78° (oxime, m.p. >290°; anil, m.p. 138°). The corresponding benzoic and cinnamic acids have been prepared from these aldehydes. H. W.

**Gallaldehyde tribenzyl ether.** R. O. Clinton and T. A. Geissman (*J. Amer. Chem. Soc.*, 1943, 65, 85—87).—Benzylation is more effectively carried out in CPhMe. 3:4:5:1-(OH)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>·CO<sub>2</sub>Me, CH<sub>2</sub>PhCl, and K<sub>2</sub>CO<sub>3</sub> in CPhMe at 140—150° give Me gallate (CH<sub>2</sub>Ph)<sub>3</sub> ether (81%), m.p. 89.5—90°. The acid gives similarly CH<sub>2</sub>Ph gallate (CH<sub>2</sub>Ph)<sub>3</sub> ether (47%), m.p. 90—90.5°. Either ester with NaOH—EtOH—H<sub>2</sub>O gives 3:4:5:1-(CH<sub>2</sub>Ph·O)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>·CO<sub>2</sub>H, m.p. 196—196.5° (lit. 187°) (resists decarboxylation), the hydrazide, m.p. 137—137.5°, of which with PhSO<sub>2</sub>Cl in C<sub>6</sub>H<sub>5</sub>N at 20—25° gives  $\alpha$ -benzenesulphon- $\beta$ -gallhydrazide (CH<sub>2</sub>Ph)<sub>3</sub> ether (88%), m.p.

165—165.5°. With Na<sub>2</sub>CO<sub>3</sub> in (CH<sub>2</sub>·OH)<sub>2</sub> at 160°, this gives gallaldehyde (CH<sub>2</sub>Ph)<sub>3</sub> ether (94%), m.p. 104—104.5° (oxime, m.p. 140—140.5°; 2:4-dinitrophenylhydrazone, m.p. 214—214.5°), which with 2:4:1-(OH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·COMe and 50% aq. KOH in boiling EtOH gives 2:4-dihydroxyphenyl 3:4:5-tribenzylloxystyryl ketone (28%), m.p. 160—161°. R. S. C.

**Formylation of methyl  $\gamma$ -resorcyate by Gattermann's reaction; synthesis of methyl 2:6-dihydroxy-3-formylbenzoate.** (Miss) K. S. Radha and R. C. Shah (*J. Indian Chem. Soc.*, 1942, 19, 393—395).—2:6:1-(OH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>Me is converted by Zn(CN)<sub>2</sub> and dry HCl in well-cooled Et<sub>2</sub>O followed by H<sub>2</sub>O into Me 2:6-dihydroxy-3-formylbenzoate (I), m.p. 113—115°; no recognisable product could be isolated after addition of AlCl<sub>3</sub>; the 2:4-dinitrophenylhydrazone and semicarbazone have m.p. 272—275° (decomp.) and 220—222°, respectively. (I), CH<sub>2</sub>Ac·CO<sub>2</sub>Et, and piperidine in C<sub>5</sub>H<sub>5</sub>N at 100° give Me 7-hydroxy-3-acetylcoumarin-8-carboxylate, m.p. 245—246°; CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> affords Et 7-hydroxy-8-carbomethoxycoumarin-3-carboxylate, m.p. 255—256°. Reduction (Zn—Hg, EtOH, dil. HCl) of (I) gives Me 2:4-dihydroxy-m-toluate, m.p. 62—63°. 2:6-Dihydroxy-3-formylbenzoic acid, m.p. 215—216°, is decarboxylated by dil. HCl at 180—190° to 2:4:1-(OH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO. (I) and conc. H<sub>2</sub>SO<sub>4</sub>—HNO<sub>3</sub> give the 5-NO<sub>2</sub>, m.p. 148—150°, and Br in AcOH affords the 5-Br-derivative, m.p. 143—145°. CO<sub>2</sub>Me in the  $\gamma$ -position has no deactivating effect on the reactivity of the resorcinol nucleus. H. W.

***p*-Alkylation of benzoyldurene by the Grignard reagent.** R. C. Fuson and B. C. McKusick (*J. Amer. Chem. Soc.*, 1943, 65, 60—64).—2:3:5:6:1-C<sub>6</sub>HMe<sub>4</sub>·COPh (I) [prep. from durene by BzCl—CS<sub>2</sub>—AlCl<sub>3</sub> (77%) or from 2:3:5:6:1-C<sub>6</sub>HMe<sub>4</sub>·COCl (II) by CdPh<sub>2</sub>], m.p. 119—120°, with CH<sub>2</sub>Ph·MgCl in Et<sub>2</sub>O gives 4'-benzyl-2:3:5:6-tetramethylbenzophenone (III), forms, m.p. 128.5—129.5° (stable) and 119—120°, and with MgBu<sup>t</sup>Cl gives 2:3:5:6-tetramethyl-4'-tert.-butylbenzophenone (IV) (33%), m.p. 127—128° [(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 212—213°, prepared by HNO<sub>3</sub> (d 1.5)]. These reactions correspond to 1:6-addition of MgRCl followed by loss of a mol. of H<sub>2</sub> or its equiv. Na—EtOH reduces (III) to 4'-benzyl-2:3:5:6-tetramethyldiphenylmethane (V), m.p. 69—70°. The Grignard reagent from *o*-C<sub>6</sub>H<sub>4</sub>Br·CH<sub>2</sub>Ph (prep. from the ketone by Martin—Clemmensen reduction) with (II) in Et<sub>2</sub>O gives 2'-benzyl-2:3:5:6-tetramethylbenzophenone (49%), m.p. 118.5—119.5°, reduced (Na—EtOH) to 2'-benzyl-2:3:5:6-tetramethyldiphenylmethane, m.p. 126.5—127.5°. 2:3:5:6:1-C<sub>6</sub>HMe<sub>4</sub>·CH<sub>2</sub>Ph [prep. from (I) by Na—EtOH but not by Clemmensen reduction], m.p. 57—58° (lit. 60.5°, 145°), with BzCl—AlCl<sub>3</sub>—CS<sub>2</sub> gives 4-benzyl-2:3:5:6-tetramethylbenzophenone (VI) (77%), m.p. 173—174°. BzCl, AlCl<sub>3</sub>, and (I) at 155° give 2:3:5:6:1:4-C<sub>6</sub>Me<sub>4</sub>(COPh)<sub>2</sub> (39%), m.p. 273—275°, reduced, as also is (VI), by Na—*n*-C<sub>5</sub>H<sub>11</sub>·OH to 4-benzyl-2:3:5:6-tetramethyldiphenylmethane, m.p. 176—177°. With boiling syrupy H<sub>3</sub>PO<sub>4</sub>, (III) gives durene and *p*-CH<sub>2</sub>Ph·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (also obtained from *p*-C<sub>6</sub>H<sub>4</sub>Bz·CO<sub>2</sub>H by Martin—Clemmensen reduction). *p*-CH<sub>2</sub>Ph·C<sub>6</sub>H<sub>4</sub>·COCl, durene, and AlCl<sub>3</sub> in CS<sub>2</sub> give impure (III), identified by reduction to (V). Reduction (Clemmensen or Na—EtOH) of (IV) gives 2:3:5:6-tetramethyl-4'-tert.-butyldiphenylmethane, m.p. 116—117°. In syrupy H<sub>3</sub>PO<sub>4</sub>, (IV) gives *p*-C<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>·CO<sub>2</sub>H and durene. (IV) is also obtained (20%) from *p*-C<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>Br by successive treatment with Mg—Et<sub>2</sub>O, anhyd. CdCl<sub>2</sub>, and (II). Br and a trace of I in boiling CCl<sub>4</sub> convert (I) into 4-bromo-2:3:5:6-tetramethylbenzophenone, m.p. 116—117°, better obtained from bromodurene by BzCl—AlCl<sub>3</sub> in CS<sub>2</sub>. (IV) gives similarly 4-bromo-2:3:5:6-tetramethyl-4'-tert.-butylbenzophenone, m.p. 182—183°, also obtained (40%) from 2:3:5:6:4:1-C<sub>6</sub>Me<sub>4</sub>Br·COPh by MgBu<sup>t</sup>Cl. R. S. C.

**Friedel—Crafts reaction with cinnamic, crotonic, and  $\beta$ -chloro-crotonic acids.** C. F. Koelsch, H. Hochmann, and C. D. Le Claire (*J. Amer. Chem. Soc.*, 1943, 65, 59—60).—CHPh·CH·CO<sub>2</sub>H and AlCl<sub>3</sub> in boiling C<sub>6</sub>H<sub>6</sub> give 3-phenylhydrindone (39%) and CHPh<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>H (25%). Adding CHMe·CH·CO<sub>2</sub>H in C<sub>6</sub>H<sub>6</sub> to AlCl<sub>3</sub> (3 mols.) and boiling gives 3-methylhydrindone (I) (81.5%), b.p. 132—137°/15 mm., and CHPhMe·CH<sub>2</sub>·CO<sub>2</sub>H (II) (4%); use of 2 mols. of AlCl<sub>3</sub> gives 50—56% of (I) and 29—32% of (II). CMeCl·CH·CO<sub>2</sub>H and AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> give 36.5% of CPhMe·CH<sub>2</sub>·CO<sub>2</sub>H (III), 58% being obtained from CPhMe·CH·CO<sub>2</sub>H, C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub>. Adding PCl<sub>5</sub> and then AlCl<sub>3</sub> to (III) in C<sub>6</sub>H<sub>6</sub> gives 78% of 3-phenyl-3-methylhydrindone (oxime, m.p. 167—168°), converted by OBU·NO—conc. HCl—EtOH at 40—45° (later room temp.) into the 2-oximino-derivative (63%), m.p. 168—168.5°, which with AcCO<sub>2</sub>H (less well, CH<sub>2</sub>O) and conc. HCl in aq. AcOH gives 3-phenyl-3-methylindane-1:2-dione, m.p. 115—116°. With *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> in EtOH, this gives the quinoxaline, m.p. 129—130°, and with H<sub>2</sub>O<sub>2</sub>—NaOH gives  $\alpha$ -phenyl- $\alpha$ -methylhomophthalic acid, m.p. 170—172°. R. S. C.

**Steric hindrance to ketonic function. II. Velocity of oximation of cyclohexanone and of its monomethyl derivatives.** A. R. Poggi [with M. Müller]. III. Velocity of oximation of 2-benzylidene-derivatives of cyclohexanone and its homologues. A. R. Poggi [with A. M. Rossi and A. Maurizi]. IV. Velocity of oximation of 2-benzyl derivatives of cyclohexanone and its homologues. A. R. Poggi

[with E. Wiechmann] (*Gazzetta*, 1942, 72, 262—273, 274—281, 282—287; cf. A., 1943, I, 132).—II. Oximes of 3- and 4-methylcyclohexanone are formed at about the same rate as that of cyclohexanone, but that of 2-methylcyclohexanone (I) is formed more slowly.

III. The oxime of 2-benzylidenecyclohexanone (II) is formed much more slowly than that of (I); oxime formation in the 4-, 5-, and 6-Me derivatives of (II) is still slower (4- > 5- > 6-).

IV. Velocity of oxime formation in  $\text{CH}_2\text{Ph}$  derivatives at 0° is intermediate between those of (I) and (II); in velocity, 2-benzyl-4-methyl- (III) > 2-benzyl-5-methyl- (IV) > 2-benzyl- (V) > 2-benzyl-6-methyl-cyclohexanone (VI). At 13°, the order is (III) and (V) > (IV) > (VI). 2- or 6-Substitution thus exerts steric hindrance. E. W. W.

#### Synthesis of 2-ketocyclohexylsuccinic acid and related substances.

I. Syntheses involving cyclohexene oxide. J. A. McRae, E. H. Charlesworth, and D. S. Alexander (*Canad. J. Res.*, 1943, 21, B, 1—12).—cycloHexene oxide (I) with  $\text{CHNa}(\text{CO}_2\text{Et})_2$  and  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  in EtOH yields a product hydrolysed and decarboxylated to 2-hydroxycyclohexylsuccinolactone, m.p. 130°, oxidised  $[\text{Br-Mg}(\text{OH})_2]$  at <10° or alkaline  $\text{KMnO}_4$  at 40—50° to 2-ketocyclohexylsuccinic acid, m.p. 154—155°, which at 200° under reduced pressure yields

2-ketohexahydrobenzofuran-3-acetic acid,  $[\text{CH}_2]_4 \begin{array}{c} \diagup \text{C}=\text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \diagdown \text{CH} \cdot \text{O} \cdot \text{CO} \end{array}$

m.p. 116—118°, and with  $\text{EtOH-NH}_3$  under pressure gives 2-ketohexahydroindole-3-acetic acid, m.p. 201°, decomposed by cold 1.25N-NaOH. 2-Hydroxycyclohexylacetolactone (Coffey, A., 1923, i, 695) is oxidised (as above) to 2-ketocyclohexylacetic acid, m.p. 73—74° (lit. 39—41°), which at 200° under reduced pressure gives 2-ketohexahydrobenzofuran, b.p. 160—165°/25 mm., m.p. 7—8° (readily hydrolysed by hot 0.1N-NaOH), and with  $\text{EtOH-NH}_3$  gives a N-containing oil (II). 2-Hydroxy- $\alpha$ -carbethoxycyclohexylacetolactone with 5N-NaOH followed by  $\text{Br-Mg}(\text{OH})_2$  yields 2-ketocyclohexylmalonic acid (III), m.p. 163° (decomp.) [semicarbazone, m.p. 271° (decomp.)], and with aq. NaOH- $\text{KMnO}_4$  gives (III) and 2-hydroxycyclohexylmalonolactone, m.p. 121—122°. With  $\text{EtOH-NH}_3$  (I) yields a product (? II) (N 21.8%).  $\alpha$ -2-Hydroxycyclohexyl- $\alpha$ -benzylacetolactone, b.p. 202—204°/10 mm. [from (I),  $\text{CHNa}(\text{CO}_2\text{Et})_2$ , and  $\text{CH}_2\text{PhCl}$  as above], is oxidised  $[\text{Br-Mg}(\text{OH})_2]$  to  $\alpha$ -2-ketocyclohexyl- $\alpha$ -benzylacetic acid, which when distilled loses 1  $\text{H}_2\text{O}$  and gives the unsaturated lactone, b.p. 220—240°/16 mm. (I) with  $\text{CHNa}(\text{CO}_2\text{Et})_2$  in EtOH, followed by MeI in  $\text{C}_6\text{H}_6$ , yields a product hydrolysed and decarboxylated to  $\alpha$ -2-hydroxycyclohexylpropiolactone, b.p. 148—150°/21 mm., oxidised  $[\text{Br-Mg}(\text{OH})_2]$  to  $\alpha$ -2-ketocyclohexylpropionic acid, m.p. 133—135°. A. Li.

Action of diazo-compounds on quinones. II. Reaction between diazo-compounds and naphthaquinones: preparation of phenyl-naphthalenes. G. B. Marini-Bettolo and C. Rossi (*Gazzetta*, 1942, 72, 208—215).—Naphthaquinone in AcOH with  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  at 60°, or better at room temp. with a trace of Cu powder, gives 2- $p$ -nitrophenyl-1:4-naphthaquinone (cf. Hey *et al.*, A., 1940, II, 211), which with Zn and  $\text{Ac}_2\text{O-NaOAc}$  gives the 1:2:4- $\text{Ac}_3$  derivative, m.p. 184°, of 1:4-dihydroxy-2- $p$ -aminophenyl-naphthalene, m.p. 165° (hydrochloride, m.p. 250°). Similarly  $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  gives 2- $m$ -nitrophenyl-1:4-naphthaquinone, m.p. 214°. Starting with 2-methyl-1:4-naphthaquinone, 3- $p$ -, m.p. 182°, and 3- $m$ -nitrophenyl-2-methyl-1:4-naphthaquinone, m.p. 225°, are obtained. The last gives the  $\text{Ac}_3$  derivative, m.p. 172°, of 1:4-dihydroxy-3- $m$ -aminophenyl-2-methylnaphthalene, m.p. indefinite, owing to oxidisability [hydrochloride, m.p. 170°, which when diazotised and coupled with  $m\text{-C}_6\text{H}_4(\text{OH})_2$  and  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$  gives compounds, m.p. 208°, and 182°, respectively]. 3- $p$ -Anisyl-2-methyl-1:4-naphthaquinone, m.p. 176° (whence 1:4-diacetoxy-3- $p$ -anisyl-2-methylnaphthalene, m.p. 115°), and 3- $p$ -tolyl-2-methyl-1:4-naphthaquinone, m.p. 158°, are prepared similarly. E. W. W.

Effects of solvents on absorption spectra of dyes.—See A., 1943, I, 114.

Derivatives of  $o$ -3'-acenaphthoylbenzoic acid. A. T. Peters and F. M. Rowe (*J. Soc. Dyers and Col.*, 1943, 59, 52—54).— $o$ -3'-Acenaphthoylbenzoic acid (I) and  $\text{AlCl}_3\text{-NaCl}$  at 134—135° (bath) give 3:4-phthaloylacenaphthene (II), m.p. 194—195° [ $p$ -nitro-, m.p. 255—256°, and 2:6-dichloro-4-nitro-phenylhydrazones, m.p. 248—249° (decomp.)], oxidised by  $\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$  to a 1:1 compound, melts partly at 258—260°, with subsequent shrinking and darkening, melting finally at 330—350°, of (II) and 4:5-phthaloylnaphthalic anhydride (III), m.p. 368° (decomp.) [ $di$ - $p$ -nitro-, m.p. 287—288° (decomp.)], and  $di$ -2:6-dichloro-4-nitro-phenylhydrazones, m.p. ~200°; imide, decomp. >390°;  $N$ -methylimide, m.p. 315—316°;  $N$ - $p$ -nitrophenylimide, m.p. ~400°; (III) is the sole product of a more vigorous similar oxidation. (III) and  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  in AcOH afford 9'-keto-3':4'-phthaloyl-8'-aza-phenalino(7':8':2:3)- $\psi$ -indole [1:2-4':5'-phthaloyl-1':8'-naphthylenebenziminazole] (IV), m.p. 380°. (I) is reduced by Zn-aq. NaOH-EtOH to  $o$ -3'-acenaphthylmethylbenzoic acid (V), m.p. 201—202°, and the lactone, m.p. 211—212°, of  $o$ -carboxyphenyl-3-acenaphthylcarbinol; (V) only is formed using Zn-aq. NaOH- $\text{CuSO}_4\text{-NH}_3$ , but subsequent cyclisation was not achieved. 4- $o$ -

Carboxybenzoylnaphthalic anhydride and 20% oleum- $\text{H}_3\text{BO}_3$  at 150°, or conc.  $\text{H}_2\text{SO}_4$  at 180—185°, afford 3:4-phthaloylnaphthalic anhydride (VI), m.p. 315° [ $p$ -nitrophenylhydrazones, m.p. 350—353° (decomp.)]; imide (VII), m.p. 360° (decomp.) (darkens from 345°);  $N$ -methylimide, m.p. 276—277°, also obtained from 4- $o$ -carboxybenzoyl-1:8-naphthal- $N$ -methylimide, m.p. 238—239°, and conc.  $\text{H}_2\text{SO}_4$  at 180—190°;  $N$ - $p$ -nitrophenylimide, m.p. >380°. 4- $o$ -Carboxybenzoyl-1:8-naphthalimide, m.p. 296—297°, and 20% fuming  $\text{H}_2\text{SO}_4$  at 160° also give (VII), but conc.  $\text{H}_2\text{SO}_4$  at 185°, 200°, or 230°, affords (VI) only. 1:2-3':4' (or 5':6')-Phthaloyl-1':5'-naphthylenebenziminazole, m.p. 320—325° (shrinks from 300°), is best prepared from (VI), a poor yield only being derived by cyclisation of 1:2-4' (or 5')- $o$ -carboxybenzoyl-1':8'-naphthylenebenziminazole, m.p. 285—287°. A. T. P.

#### IV.—STEROLS AND STEROID SAPOGENINS.

Cafesterol. II. H. Hauptmann and J. França (*J. Amer. Chem. Soc.*, 1943, 65, 81—85; cf. A., 1939, II, 367).—Cafesterol (I) is purified as solvate, +MeOH (lost at 120°), m.p. 156—158°, and then has  $[\alpha]_D^{25} -114^\circ$ ; its m.p. is a poor criterion of purity. Its inert O is probably present in an ether group.  $\text{Al}(\text{OPr}^i)_3\text{-Pr}^i\text{OH}$  is without effect. Its acetate with  $\text{H}_2\text{-Raney Ni}$  in EtOH at 25°/696 mm. yields an oxcafestanediol acetate (60%), m.p. 156°, colourless in  $\text{C}(\text{NO}_2)_4$  and unaffected by  $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  (II) or dil. acid, but hydrolysed by hot  $\text{KHCO}_3\text{-MeOH-H}_2\text{O}$  to oxcafestanediol (III), m.p. 188°. Cafestanetriol, m.p. 227°,  $[\alpha]_D^{25} -33.7^\circ$  in EtOH, and  $\text{HIO}_4\text{-MeOH}$  give  $\text{CH}_2\text{O}$ . With boiling  $\text{Ac}_2\text{O-C}_6\text{H}_5\text{N}$ , (I) gives oxcafestatrienol acetate (IV), m.p. 114°,  $[\alpha]_D^{25} -78.5^\circ$  in  $\text{CHCl}_3$  (absorption spectrum given), which absorbs 2 O from (II), absorbs 4  $\text{H}_2$  in presence of  $\text{PtO}_2$  in AcOH (to give a syrup, hydrolysed to an oil, which is stable to  $\text{HIO}_4$ ), but absorbs 2  $\text{H}_2$  in presence of Raney Ni in EtOH at 27°/703.6 mm. No adduct is obtained from (I) and  $(\text{CH}\cdot\text{CO})_2\text{O}$  at 135°. (III) and its isomeride, (I), and (IV) have no androgenic or cortenic activity. R. S. C.

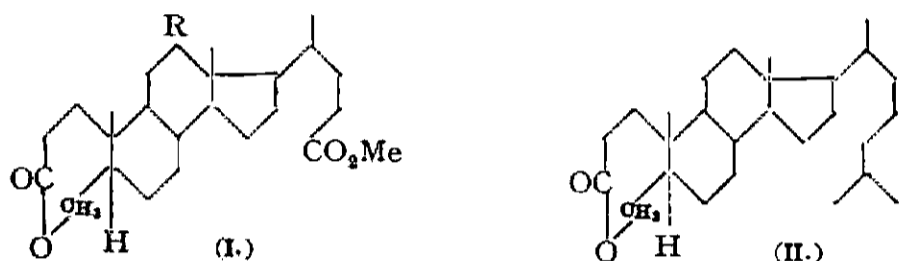
Acyl migration in sterols. V. A. Petrow, O. Rosenheim, and W. W. Starling (*J.C.S.*, 1943, 135—139; cf. A., 1937, II, 191).—A very facile acyl migration, without analogy in the steroid series, but similar to that in glycerides, occurs in the monoesters of  $cis$ - $\Delta^5$ -cholestene-3:4-diol (I); intermediate formation of orthocarbonic esters is probable, and other mechanisms are discussed. Cholesteryl dibromide (II) and  $\text{AgOAc-C}_6\text{H}_5\text{N-Et}_2\text{O}$  followed by  $\text{CHCl}_3\text{-AcOH}$  give, after decomp. of its 1:1 AcOH compound, m.p. 142—144° (softens at 124°), with boiling 85% EtOH, 4-acetoxy- $\Delta^5$ -cholesten-3-ol (III), m.p. 164—165°,  $[\alpha]_D^{25} -88.8^\circ$ ,  $[\alpha]_{461}^{25} -107.8^\circ$  (1:1  $\text{EtCO}_2\text{H}$  compound, solvent lost at 120°). Cholesteryl acetate and  $\text{SeO}_2\text{-95\% AcOH}$  in  $\text{C}_6\text{H}_6$  or dioxan also give (III) and ~5% of 3-acetoxy- $\Delta^5$ -cholesten-4-ol (IV). (IV) is converted into (III) by AcOH in dioxan at 90°, or in boiling  $\text{C}_6\text{H}_6$ . The acetates, m.p. 165° and 191°, of Marker *et al.* (A., 1940, II, 17) are (III) and (IV), respectively, and the so-called 3-acetates of 4-hydroxy-sitosterol and -stigmasterol (Marker *et al.*, A., 1938, II, 276) are similarly the  $cis$ -3:4-diol 4-monoacetates. (II) and  $\text{EtCO}_2\text{Ag-C}_6\text{H}_5\text{N-Et}_2\text{O}$  give 4-propionyloxy- $\Delta^5$ -cholesten-3-ol (V), m.p. 134—135°,  $[\alpha]_D^{25} -87.8^\circ$  (AcOH compound, m.p. 110—112°), also obtained from cholesteryl propionate and  $\text{SeO}_2\text{-C}_6\text{H}_6\text{-95\% AcOH}$ . Acetylation of (V) or propionylation of (IV) gives 3-acetoxy-4-propionyloxy- $\Delta^5$ -cholestene, m.p. 156—157°,  $[\alpha]_D^{25} -96.5^\circ$ . 4-Butyryloxy- $\Delta^5$ -cholesten-3-ol, m.p. 125—126°,  $[\alpha]_D^{25} -75.3^\circ$  (AcOH compound, m.p. 99—100°), and 3-acetoxy-4-butyryloxy- $\Delta^5$ -cholestene, m.p. 139—140°,  $[\alpha]_D^{25} -90.8^\circ$ , are also prepared. 4-Benzoyloxy- $\Delta^5$ -cholesten-3-ol, m.p. 154—155°,  $[\alpha]_D^{25} -29.5^\circ$  [identical with compound C of Spring *et al.* (A., 1939, II, 477)], is acetylated to 4-benzoyloxy-3-acetoxy- $\Delta^5$ -cholestene, new m.p. 132—134°,  $[\alpha]_D^{25} -59.5^\circ$ , also obtained by benzoylating the 3-monoacetate.  $\Delta^5$ -Androsten-3( $\beta$ )-ol-17-one and  $\text{Br-CHCl}_3$  afford a product, which with  $\text{AgOAc-C}_6\text{H}_5\text{N-Et}_2\text{O}$  gives 4-acetoxy- $\Delta^5$ -androsten-3( $\beta$ )-ol-17-one, m.p. 192—193°,  $[\alpha]_D^{25} -60.7^\circ$ , hydrolysed to  $cis$ - $\Delta^5$ -androsten-3:4-diol-17-one, m.p. 204—205°,  $[\alpha]_D^{25} -28.5^\circ$ . Cholesteryl acetate and  $\text{SeO}_2$  in aq. dioxan afford (IV), also obtained by partial conversion of (III) by AcOH-dioxan (1:1) at 90°. Cholesteryl benzoate similarly gives 3-benzoyloxy- $\Delta^5$ -cholesten-4-ol (VI). (I), (III), or (IV) with boiling AcOH (5 min.) affords (after acetylation) 3:6-diacetoxy- $\Delta^4$ -cholestene (VII) and thence the diol. (IV) and  $\text{SOCl}_2\text{-Et}_2\text{O-C}_6\text{H}_5\text{N}$  at room temp., or by gentle refluxing, give 4-chloro-3-acetoxy- $\Delta^5$ -cholestene (VIII), m.p. 108—109°,  $[\alpha]_D^{25} -70.4^\circ$ , also obtained from 6-chloro-3-acetoxycholestan-5-ol and cold  $\text{SOCl}_2\text{-C}_6\text{H}_5\text{N}$ . (VIII) and  $\text{KOAc-dioxan-AcOH}$  at 100° (bath) yield the AcOH compound of (III); (VIII)- $\text{KOAc-AcOH}$  at 90° and then at the b.p., followed by acetylation, afford (VII). (VI) and  $\text{SOCl}_2\text{-Et}_2\text{O-C}_6\text{H}_5\text{N}$  give 4-chloro-3-benzoyloxy- $\Delta^5$ -cholestene, m.p. 127—128°,  $[\alpha]_D^{25} -81.9^\circ$ , identical with the 6-chloro-3-benzoyloxy- $\Delta^4$ -cholestene prepared from 6-chloro-3-benzoyloxycholestan-5-ol (cf. Spring *et al.*, loc. cit.). (I) is converted by boiling  $\text{Et}_2\text{O-C}_6\text{H}_5\text{N}$  (1 mol.)- $\text{SOCl}_2$  (1 mol.) into its endo-sulphite, m.p. 146—148° (decomp.),  $[\alpha]_D^{25} -64.6^\circ$ ; (III) similarly affords  $di$ -(4-acetoxycholesteryl) sulphite, m.p. 159—160°,  $[\alpha]_D^{25} -106.1^\circ$ .  $[\alpha]$  are in  $\text{CHCl}_3$ . A. T. P.

**Action of *B. coli* on dehydronorcholene.** A. Butenandt and H. Dannenberg (*Naturwiss.*, 1942, **30**, 585—586).—The oxidation of dehydronorcholene to 22-ketodehydronorcholene is not as previously reported (A., 1942, II, 364) due to the action of *B. coli*, but is an autoxidation, since it proceeds to the same extent in sterile Sauton medium without addition of the bacteria. J. H. B.

**Attempted asymmetric syntheses employing choleic acids.**—See A., 1943, II, 159.

**Catalytic reduction of dehydrocholic acid in presence of Raney nickel.** W. M. Hoehn and H. E. Ungnade (*J. Amer. Chem. Soc.*, 1943, **65**, 124).—Dehydrocholic acid and  $H_2$ -Raney Ni in MeOH at 105°/3800 lb. give reductodehydrocholic acid (67—85%), its Me ester (up to 20%), and Me dehydrocholate (up to 12%). R. S. C.

**Bile acids and related substances. XVII. Formation of lactones from ketones and perbenzoic acid.** V. Burckhardt and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 1434—1443; cf. A., 1942, II, 411).—Me 3-keto-12( $\beta$ )-acetoxycholanate is oxidised by  $BzO_2H$  in  $CHCl_3$  at 18° to the lactone (I) ( $R = OAc$ ), m.p. 187—190°; under similar conditions Me 12-keto-3( $\alpha$ )-acetoxycholanate remains unchanged. Coprostan-3-one gives the lactone,  $C_{27}H_{46}O_2$ , m.p. 155—157°,  $[\alpha]_D^{20} + 49.2 \pm 2^\circ$  in  $COMe_2$ , identical with the compound of Gardner *et al.* (A., 1914, i, 169). Me 3-ketocholanate yields the lactone (I) ( $R = H$ ), m.p. 130—133°,  $[\alpha]_D^{18} + 50.0 \pm 4^\circ$  in  $COMe_2$ , converted

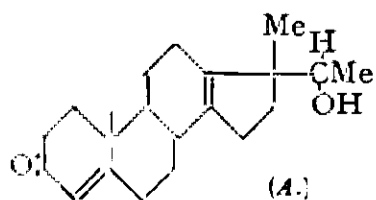


by hydrolysis, methylation, oxidation, and renewed methylation into  $Me_3$  lithobilianate, m.p. 108—110°. Cholestanone gives the lactone (II), m.p. 186—187°,  $[\alpha]_D^{18} + 1.2 \pm 2^\circ$  in  $COMe_2$ , degraded to the "dihydro-Diels' acid" (cf. Windaus, A., 1919, i, 203). *allo*-Pregnan-3( $\alpha$ )-ol-20-one acetate does not react whereas the 3( $\beta$ )-compound gives (after hydrolysis) androstane-3( $\beta$ ):17( $\alpha$ )-diol in small yield. M.p. are corr. (block; limit of error  $\pm 2^\circ$ ). H. W.

**Bile acids and related substances. XVIII. Simplified preparation of methyl  $\Delta^{11}$ -cholates by thermal fission of 12-benzoyloxy-derivatives.** A. Lardon, P. Grandjean, J. Press, H. Reich, and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 1444—1452).—Me 12( $\beta$ )-hydroxycholanate is converted by  $BzCl$  and  $C_5H_5N$  at room temp. and then at 100° into the non-cryst. benzoate,  $[\alpha]_D^{25} + 57.3 \pm 1^\circ$  in  $COMe_2$ , which loses  $H_2O$  at 320°/11 mm. giving Me  $\Delta^{11}$ -cholenate, needles, m.p. 61—61.5°, or leaflets, m.p. 56—58°. Similarly Me 3-keto-12( $\beta$ )-benzoyloxycholanate (I), a glassy solid,  $[\alpha]_D^{25} + 54.3 \pm 3^\circ$  in  $COMe_2$ , affords Me 3-keto- $\Delta^{11}$ -cholenate, m.p. 121—123°. Me 12( $\beta$ )-hydroxy-3( $\alpha$ )-acetoxycholanate gives the corresponding benzoate, m.p. 114—115°,  $[\alpha]_D^{18} + 71.65 \pm 2^\circ$  in  $COMe_2$ , hydrolysed by  $K_2CO_3$  in aq. MeOH at room temp. to the non-cryst. 3( $\alpha$ )-hydroxy-12( $\beta$ )-benzoyloxycholanate [non-cryst. Me ester (II)] and converted at 250°/vac. into Me 3( $\alpha$ )-acetoxymethyl- $\Delta^{11}$ -cholenate, m.p. 117—118°, and, probably, Me choladienate, m.p. 75—76°. Oxidation of (II) by  $CrO_3$  in AcOH gives (I). M.p. are corr. (block). H. W.

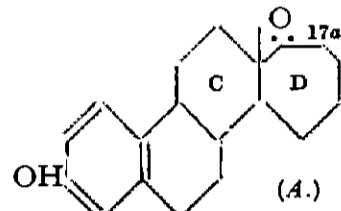
**Steroid ketones.**—See B., 1943, III, 110.

**Steroids and sex hormones. LXXXII. Rearrangement of 17 : 20-oxido- $\Delta^4$ -pregnen-3-one by acetic acid.** L. Ruzicka, M. W. Goldberg, and E. Hardegger (*Helv. Chim. Acta*, 1942, **25**, 1680—1689).—17 : 20-Oxido- $\Delta^4$ -pregnen-3-one (I) (isomeride B; cf. A., 1943, II, 96) is converted by AcOH at room temp. into an unsaturated CO-alcohol (II),  $C_{21}H_{30}O_2$ , m.p. 125.5—126.5°,  $[\alpha]_D + 30.5^\circ$  in  $CHCl_3$  (also  $+0.5COMe_2$ ) [semicarbazone, m.p. 213—214°], which gives an intense yellow colour with  $C(NO_2)_4$ . (II) is converted by  $Ac_2O-C_5H_5N$  at room temp. into its acetate (III), m.p. 172°,  $[\alpha]_D + 58.7^\circ$  in  $CHCl_3$  (also  $+0.5H_2O$ ), also obtained together with a by-product,  $C_{23}H_{32}O_4$ , m.p. 136°, by the action of  $Ac_2O-ZnCl_2$  on (I). (II) is oxidised by  $o-CO_2H \cdot C_6H_4 \cdot CO_2H$  in  $CHCl_3$  to a compound,  $C_{21}H_{30}O_3$ , m.p. 162° (softens at 159°) (acetate, m.p. 148—149°), whereas (III) yields a compound,  $C_{23}H_{32}O_4$ , m.p. 220—221°. (II) is oxidised by  $OsO_4$  to a  $\Delta^4$ -3-ketotriol,  $C_{21}H_{32}O_4$ , m.p. 227—228° (monoacetate), which is saturated towards  $C(NO_2)_4$  and does not yield well-defined products with  $HIO_4$ ; (III) is scarcely attacked by  $OsO_4$ . Hydrogenation of (II) leads to the absorption of 3  $H_2$  and the saturated [towards  $C(NO_2)_4$ ] product is oxidised by  $CrO_3$  to a saturated diketone,  $C_{21}H_{32}O_2$ , m.p. 80—80.5°,  $[\alpha]_D + 4^\circ$  in  $CHCl_3$ . When treated similarly (III) affords an acetoxyketone,  $C_{23}H_{36}O_3$ , m.p. 116—117°,  $[\alpha]_D + 14.3^\circ$  in  $CHCl_3$ , converted (Wolff-Kishner) into the saturated alcohol,  $C_{26}H_{36}O$ , m.p. 119°,  $[\alpha]_D + 25^\circ$  in  $CHCl_3$ . Structure (A) is tentatively assigned to (II). M.p. are corr. (vac.). H. W.



**Steroids and sex hormones. LXXX. Constitution of D-homo-œstrone.** M. W. Goldberg and S. Studer (*Helv. Chim. Acta*, 1942, **25**, 1553—1556; cf. A., 1941, II, 257).—17-Hydroxymethylene-D-homo-œstrone 3-Me ether is oxidised by  $CrO_3$  in AcOH at room temp. to 7-methoxy-2-methyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-phenanthrene-2-carboxylic-1- $\beta$ -propionic acid, m.p. 251—258°,  $[\alpha]_D + 76 \pm 4^\circ$  in dioxan ( $Me_2$  ester, m.p. 83.5—84°,  $[\alpha]_D + 73 \pm 3^\circ$  in dioxan) (cf. Bardhan, A., 1937, II, 63). The spatial arrangement of rings c and d in D-homo-œstrone is therefore the same as that in œstrone. M.p. are corr. (vac.). H. W.

**Steroids and sex hormones. LXXXI. D-Bishomoœstrone.** M. W. Goldberg and S. Studer (*Helv. Chim. Acta*, 1942, **25**, 1556—1560; cf. A., 1941, II, 257).—D-Homoœstrone is converted by  $BzCl$  in 7%  $KOH-C_5H_5N$  at room temp. and then at  $\sim 60^\circ$  into the benzoate (I), m.p. 161—162°,  $[\alpha]_D + 23.2 \pm 2^\circ$  in dioxan, transformed by KCN in EtOH-AcOH at room temp. into the cyanohydrin, m.p. 182—184° with loss of HCN, which with  $Ac_2O-C_5H_5N$  at 100° yields the corresponding acetate, m.p. 220—221°. D-Homoœstrone acetate and KCN in EtOH-AcOH at room temp. give the cyanohydrin (II), m.p. 199—200°. In the production of (I) and (II) there is no appreciable production of any epimeride. Hydrogenation ( $PtO_2$  in AcOH) of (II) and treatment of the product with  $HNO_2$  yields D-bishomoœstrone acetate, m.p. 149—151°,  $[\alpha]_D - 37.1 \pm 2^\circ$  in dioxan, hydrolysed by boiling  $KOH-MeOH$  to D-bishomoœstrone [3-hydroxy- $\Delta^{1:3:5}$ -D-bishomoœstratrien-(17b)-one] (A), m.p. 290—292°,  $[\alpha]_D - 34.8 \pm 4^\circ$  in dioxan (oxime, m.p. 174—176°). In (A) O may be at 17a. M.p. are corr. (vac.). H. W.



## V.—TERPENES AND TRITERPENOID SAPOGENINS.

**Structure of ketonic complexes of carvone.**—See A., 1943, I, 116.

**Physical properties of terpenes. I. System  $\alpha$ - and  $\beta$ -pinene.** R. E. Fugitt, W. D. Stallcup, and J. E. Hawkins (*J. Amer. Chem. Soc.*, 1942, **64**, 2978—2981).— $d$ ,  $n$ , and  $\alpha$  are recorded for  $\alpha$ - and  $\beta$ -pinene and their mixtures, as are v.p.-temp. relations for  $\alpha$ - and  $\beta$ -pinene at 15—80 mm. and vapour-liquid composition data for mixtures at 20 mm. R. S. C.

**Decomposition of pernitrosoketones. II. Pernitrosophenone and pernitrosomenthone.** A. Gandini (*Gazzetta*, 1942, **72**, 232—241).—Pernitrosophenone (I) in heavy paraffin at 150—160° decomposes to a mixture of  $\alpha$ - and  $\beta$ -fencholenitrile (also obtained by decomp. of fenchoneoxime), and a resinous product (II), similar to that obtained from pernitrosocamphor (III) (cf. A., 1943, II, 137). (III) contains a substance,  $C_{15}H_{16}O_2N_2$  (IV) [isomeric with, but more stable than, (I)], in which the  $N \cdot NO_2$  group is regarded as *cis* to the bridge- $CH_2$ , as compared with a *trans*-structure in (I). At  $> 200^\circ$ , (IV) decomposes, as (I). If the decomp. of (III) in heavy paraffin at 150° is interrupted after evolution of gas, camphornitroimine (?),  $C_{10}H_{18}O_2N_2$ , m.p. 57—58°, is isolated. Pernitrosomenthoneoxime in heavy petroleum at 150—160° gives menthonenitrile. The pernitroso-derivative from the oily oxime of *d*-menthone gives a product which is hydrolysed to a substance,  $C_{10}H_{18}ON$ , m.p. 128°. E. W. W.

**Sesquiterpenes. LVII. Crystallised cadinol from Java oil of lemon.** P. A. Plattner and R. Márkus (*Helv. Chim. Acta*, 1942, **25**, 1674—1679).—Treatment of the most volatile portions of a residual fraction of the oil with  $p-NO_2 \cdot C_6H_4 \cdot COCl$  and  $C_5H_5N$  gives a *p*-nitrobenzoate, m.p. 136°,  $[\alpha]_D - 6.76^\circ$  in  $CHCl_3$ , hydrolysed by  $KOH-MeOH$  to cadinol (I),  $C_{15}H_{26}O$ , m.p. 72.5°,  $[\alpha]_D - 39.8^\circ$  in  $CHCl_3$ . (I) with  $KHSO_4$  at 150—180° gives cadinene, b.p. 108—112°/12 mm. (dihydrochloride, m.p. 117.5°), dehydrogenated ( $Pd-C$  at 275—350°) to cadalene. (I) is hydrogenated (Raney Ni in EtOH at 18.5°) to dihydrocadinol, m.p. 124.5°,  $[\alpha]_D - 72.5^\circ$  in  $CHCl_3$ . It is stable towards  $CrO_3$ , indicating the presence of *tert*. OH; characteristic products are not obtained by its direct oxidation or by ozonisation of its dehydrogenation product. M.p. are corr. H. W.

**Triterpenes. LXXI. Attempted transformation of quinovic acid into triterpene derivatives poorer in oxygen.** L. Ruzicka and A. Marxer (*Helv. Chim. Acta*, 1942, **25**, 1561—1571).—Acetylquinovyldichloride, m.p. 193—194°, obtained from the acid and  $SOCl_2$  in hexane, is reduced (Rosenmund) at various temp. to acetylnorquinovadienol (I),  $C_{31}H_{46}O_3$ , m.p. 162—164°, with some norquinovadienolcarboxylic acid characterised as the Me ester of the acetylated acid, m.p. 175—177°,  $[\alpha]_D - 45.5^\circ$  in  $CHCl_3$ . Reduction (Wolff-Kishner) of the semicarbazone, m.p. 275—276°, of (I) yields two isomeric norquinovadienols,  $C_{29}H_{44}O$ , m.p. 197—199°,  $[\alpha]_D - 55^\circ$  in  $CHCl_3$  [acetate, m.p. 187—188°;  $H_2$ -compound, m.p. 159—160°,  $[\alpha]_D - 66^\circ$  in  $CHCl_3$ ; gives a yellow colour with  $C(NO_2)_4$ , and m.p. 88—90°,  $[\alpha]_D - 31^\circ$  in  $CHCl_3$  (acetate, m.p. 152—155°,  $[\alpha]_D - 34.8^\circ$  in  $CHCl_3$ ), respectively which does not absorb  $H_2$ , together with norquinovadienediol,  $C_{29}H_{46}O_2$ , m.p. 166—169°. Novyl chloride, m.p. 209—212° (decomp.), is reduced ( $Pd-BaSO_4$  in boiling xylene) to

*nova-aldehyde*, m.p. 197—201°; the *semicarbazone*, m.p. 256—258°, is converted (Wolff-Kishner) into a neutral *lactone*,  $C_{30}H_{46}O_2$ , m.p. 157—160°,  $[\alpha]_D^{25} +398^\circ$  in  $CHCl_3$ , which could not be hydrolysed satisfactorily by 3N-KOH-MeOH at 175—180° or by HBr-AcOH at 120°. *Acetylpyroquinovyl chloride*, m.p. 160—163°, is reduced (Rosenmund) to *acetylnorquinovenolal*, m.p. 170—173°, which gives a *semicarbazone*, m.p. 271—273°, transformed (Wolff-Kishner) into *norquinovenol* (II), m.p. 86—90°,  $[\alpha]_D^{25} -84^\circ$  in  $CHCl_3$  (acetate, m.p. 167—169°,  $[\alpha]_D^{25} -66^\circ$  in  $CHCl_3$ ); this is dehydrogenated by Se at 345° to 1:2:8-trimethylpicene, m.p. 308—310°.  $Me_2$  quinovate is oxidised ( $CrO_3$  in AcOH) to  $Me_2$  quinovenonedicarboxylate, m.p. 149—150°, the *semicarbazone*, m.p. 175—180°, softens at ~150°, of which is reduced (Wolff-Kishner) to *quinovenedicarboxylic acid*, m.p. 310—314°. M.p. are corr. H. W.

**Triterpenes. LXXII. Aescigenin**, the aglucon of the saponin from the seeds of the horse chestnut [*Aesculus hippocastanum*, L.]. L. Ruzicka, W. Janett, and E. Rey (*Helv. Chim. Acta*, 1942, 25, 1665—1673).—The finely-divided seeds are extracted successively with 2.5% NaOH and  $H_2O$ ; the residue yields to 65% EtOH crude aescin, m.p. 200—210°, in 2% yield. This when hydrolysed with 5% HCl-EtOH at 100° for 72 hr. gives aescigenin (I),  $C_{35}H_{58}(OH)_8O_8$ , m.p. 311—312°,  $[\alpha]_D^{25} +46^\circ$  in EtOH, which can be purified by crystallisation from EtOH or through the penta-acetate (II), m.p. 206—207°,  $[\alpha]_D^{25} +60^\circ$  in  $CHCl_3$ . (I) contains 5 OH (Zerevitinov) and according to its spectrum  $>CO$ , which cannot be detected by chemical means. (I) is therefore not an ester of tiglic acid. (I) gives a positive colour test with  $C(NO_2)_4$  but attempts to hydrogenate (II) using  $PtO_2$  in AcOH at room temp. or with  $H_2$  at 175°/90 atm. or to reduce (I) by Na in EtOH were unsuccessful. Mild oxidation of (II) by  $CrO_3$  in AcOH yields an  $\alpha\beta$ -unsaturated *keto-aescigenin penta-acetate*,  $C_{45}H_{84}O_{12}$  (based on  $C_{35}H_{56}O_6$ ), m.p. 222—223.5°,  $[\alpha]_D^{25} +54^\circ$  in  $CHCl_3$ , which does not give a colour with  $C(NO_2)_4$ . Hence (I) contains only one double linking. M.p. are corr. H. W.

**Essential oil of Cupressus macrocarpa**.—See B., 1943, III, 62.

**Sapogins and sapogenins. XX. Colour reactions of triterpenoid sapogenins.** C. R. Noller, R. A. Smith, G. H. Harris, and J. W. Walker (*J. Amer. Chem. Soc.*, 1942, 64, 3047—3049; cf. A., 1941, II, 370).—Characteristic colours or series of colour changes are produced by dissolving triterpenoids in  $SOCl_2$  containing traces of  $SnCl_4$  (0.01%; 21 examples),  $FeCl_3$  (0.01%; 5 examples),  $SbCl_3$  (0.01%; 6 examples),  $PbCl_2$  (0.01%; 6 examples),  $POCl_3$  (10%) +  $H_2O$  (0.5%) (6 examples),  $SnCl_4$  (0.01%) +  $FeCl_3$  (0.005%) (6 examples),  $H_3PO_4$ , or  $H_2SO_4$ . Commercial  $SOCl_2$  sometimes contains enough metal to give the colours. Pure  $SOCl_2$  sometimes gives colours (7 examples). Colours are not given by pure  $POCl_3$ ,  $PbCl_2$ ,  $PbCl_4$ ,  $SiCl_4$ ,  $Cl_2$ ,  $SO_2$  or HCl in  $SOCl_2$ , or by  $SnCl_4$  in  $C_6H_6$ , light petroleum,  $CHCl_3$ , or cyclohexane. R. S. C.

## VI.—HETEROCYCLIC.

**Tetrahydrofurfuryl alcohols**.—See B., 1943, II, 113.

**Coumaran series.** R. T. Arnold and J. Moran (*J. Amer. Chem. Soc.*, 1942, 64, 2986—2988).—2:4:1-(OH) $\cdot C_6H_3(OMe)\cdot CO_2Me$ , m.p. 49—51°,  $CH_2\cdot CH\cdot CH_2Cl$ ,  $K_2CO_3$ , and NaI in boiling  $COMe_2$  give *Me 4-methoxy-2-allyloxybenzoate* (I), m.p. 49—50°, which in boiling  $NPhMe_2-N_2$  gives *Me 2-hydroxy-4-methoxy-3-allylbenzoate* (II), m.p. 57—59° (reddish-violet with  $FeCl_3$ ). With HBr-AcOH at 100° and then boiling, aq. NaOH, (II) gives 3-hydroxy-1-methyl-1:2-dihydrobenzofuran-4-carboxylic, m.p. 155—156° (red  $FeCl_3$  colour; Me ester), and 3-methoxy-1-methyl-1:2-dihydrobenzofuran-6-carboxylic acid (III), m.p. 207—208°. With dry HBr- $CHCl_3$  and a trace of  $FeCl_3$  at 0° and later room temp., (II) gives *Me 2-hydroxy-4-methoxy-3- $\beta$ -bromon-propylbenzoate* (IV), m.p. 73—74°, and some (III). Aq. NaOH at room temp. and later the b.p. converts (IV) into (III). The acid derived from (I) in boiling  $NPhMe_2$  gives  $CO_2$  and 2:4:1-(OH) $\cdot C_6H_3(OMe)\cdot CH_2\cdot CH\cdot CH_2$ , an oil (positive  $FeCl_3$  test), identified by conversion into 2:4:1-(OMe) $\cdot C_6H_3\cdot CO_2H$  by successive methylation, isomerisation by alkali, and oxidation. Attempts at cleavage of (III) by HBr gave red polymerides. R. S. C.

**Styrylchromones.** G. B. Marini-Bettolo (*Gazzetta*, 1942, 72, 201—208).—2:4:1-(OH)(OMe) $\cdot C_6H_3\cdot COMe$  in EtOH with  $CHPh\cdot CH\cdot CHO$  ( $C_5H_5N$ ) gives 2-hydroxy-4-methoxy- $\alpha$ -cinnamylidenacetophenone (I), m.p. 147°. From the appropriate ketones 2-hydroxy-3:4-dimethoxy- (II), -4:5-dimethoxy- (III), m.p. 153°, and 2:4-dimethoxy- (IV), m.p. 98°, and 2:4:5-trimethoxy- $\alpha$ -cinnamylidenacetophenone (V), m.p. 110°, are prepared similarly [using 50% NaOH for (IV) and (V)]. With  $SeO_2$  in boiling  $C_6H_{11}OH$  (16 hr.), (I) gives 7-methoxy-, (II) 7:8-dimethoxy-, and (III) 6:7-dimethoxy-2-styrylchromone, m.p. 184°. By the reaction of Algar and Flynn (A., 1934, 1226), (I) and its analogues give with KOH-EtOH- $H_2O_2$  (10 min. at 100°) 7-methoxy-, m.p. 221°, 7:8-dimethoxy-, m.p. 248°, and 6:7-dimethoxy-2-styrylchromonol, m.p. 237°, all strongly fluorescent. Since (IV) and (V) with NaOH-MeOH- $H_2O_2$  give  $\beta$ -2:4-dimethoxy-, m.p. 113°, and  $\beta$ -2:4:5-trimethoxy-benzoyl- $\alpha$ -styrylethylene oxide, m.p. 120° (cf. Weitz *et al.*, A., 1921, i, 868), it is suggested that Algar

and Flynn's reaction proceeds through a similar intermediate ethylene oxide stage. E. W. W.

**Benzopyrone series. VII. Stages in the synthesis of karanjin.** T. R. Seshadri and V. Venkateswarlu (*Proc. Indian Acad. Sci.*, 1943, 17, A, 16—19; cf. A., 1941, II, 330).—The condensation product of 2:6:1-(OH) $\cdot C_6H_3\cdot CHO$  with  $CH_2Br\cdot CO_2Et$  and NaOEt was hydrolysed to 3-hydroxy-2-aldehydophenoxyacetic acid, m.p. 176—177°, which with NaOAc and  $Ac_2O$  at 150° yields 4-hydroxy-coumarone (cf. Reichstein and Hirt, A., 1933, 281). F. R. G.

**Constitution of natural coumarins of Toddalia aculeata.** P. Dutta (*J. Indian Chem. Soc.*, 1942, 19, 425—434).—Extraction of the stem bark with  $Et_2O$  gives a substance,  $C_{16}H_{16}O_4$ , m.p. 238—239°, neutral to litmus and indifferent to  $FeCl_3$ , in very small amount, *aculeatin* (I), m.p. 113° (corr.),  $[\alpha]_D^{25} -16.8^\circ$  in EtOAc, and *aculeatin hydrate* (II), m.p. 150° (corr.),  $[\alpha]_D^{25} +50.9^\circ$  in  $CHCl_3$ , also obtained from (I) by prolonged treatment with dil.  $H_2SO_4$  at 100°. (I) contains 2 OMe and behaves as a lactone, being hydrolysed by alkali in presence of a trace of  $HgO$  to the stable acid,  $C_{16}H_{22}O_7$ , m.p. 171°. (I) does not condense with the usual reagents for

aldehydes or ketones but an oxide ring is present since (I) is convertible into (II). (I) is therefore A ( $R = \cdot CH_2\cdot CH\cdot CMe_2$ ). (II) gives a diacetate, m.p. 127°, hydrolysed by alkali to (II), and a *H phthalate*, m.p. 204°, so that 1 OH is probably *tert*. When oxidised by  $CrO_3$  (II) yields  $COMe_2$ . Oxidation (Criegee) of (II) leads to an aldehyde,  $C_{13}H_{12}O_6$ , m.p. 142—142.5° (corr.) (*p*-nitrophenylhydrazones, m.p. 213°), which reduces  $Ag_2O\cdot NH_3$ ; hence (II) is an  $\alpha\beta$ -glycol [A;  $R = \cdot CH_2\cdot CH(OH)\cdot CMe_2\cdot OH$ ]. (I) is converted by fused  $ZnCl_2$  at 140—145° and (II) by dil. HCl at 140° into a ketone,  $C_{16}H_{18}O_5$ , m.p. 119—120° (corr.) (*semicarbazone*, m.p. 209°; *p*-nitrophenylhydrazones, m.p. 210°). The aldehyde and ketone are also obtained from toddalolactone (III) (A., 1938, II, 451). Chemical evidence is definitely in favour of the identity of (II) and (III). H. W.

**Aluminium chloride, a new reagent for the condensation of  $\beta$ -ketonic esters with phenols. VI. Condensation of resacetophenone with ethyl  $\alpha$ -alkylacetoacetates.** C. V. Deliwala and N. H. Shah (*Proc. Indian Acad. Sci.*, 1943, 17, A, 7—10; cf. A., 1941, II, 332).—2:4:1- $C_6H_3(OH)_2\cdot COMe$  condenses with  $CHMeAc\cdot CO_2Et$  in presence of  $AlCl_3$  in  $PhNO_2$  to yield 5-hydroxy-6-acetyl-3:4-dimethylcoumarin (*Ac* derivative, m.p. 105—106°; *oxime*, m.p.  $\leq 245^\circ$ ); with  $Me_2SO_4$  this gives 2:6-dimethoxy-3-acetyl- $\alpha\beta$ -dimethylcinnamic acid, m.p. 158—159°, and is converted by Kostanecki acetylation into 3'-acetyl-2':3:4-trimethylchromono-7':8':6:5- $\alpha$ -pyrone. Similarly were prepared 5-hydroxy-6-acetyl-4-methyl-3-ethyl-, m.p. 158—159° (*Ac* derivative, m.p. 119—120°), and -6-acetyl-3-benzyl-4-methylcoumarin, m.p. 186—187° [*Ac* derivative, m.p. 147—148°; *oxime*, m.p. 250—251° (decomp.)], which is converted (Kostanecki) into 3'-acetyl-3-benzyl-2':4-dimethylchromono-7':8':6:5- $\alpha$ -pyrone, m.p. 181—182°. No condensation occurs with  $CHRAc\cdot CO_2Et$  where R is  $Pr^a$ , allyl, or Cl. F. R. G.

**Pigments of the flowers of Hibiscus sabdariffa. Sabdaretin, new hydroxyflavone.** P. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, 16, A, 323—327; cf. A., 1942, II, 327).—The EtOH extract of the petals, after separation of hibiscitrin and gossypitrin, on pptn. with basic Pb acetate yields *sabdaritrin*,  $C_{21}H_{20}O_{14}\cdot 3H_2O$ , m.p. 251—253° (decomp.), hydrolysed (7%  $H_2SO_4$ ) to a hydroxyflavone, *sabdaretin*,  $C_{15}H_{10}O_8\cdot 3H_2O$ , m.p.  $\leq 360^\circ$  (shrinks at 300°) [acetate, m.p. 198—200° (decomp.; sinters ~160°)], colour reactions of which are given. A. Li.

**Chemical components of Indian tulip (Thespesia populnea) flowers.** K. Neelakantam, P. S. Rao, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1943, 17, A, 26—31; cf. A., 1938, II, 394).—The three yellow pigments of the flower petals (cf. Rao and Reddy, A., 1941, III, 405) are accompanied by the colourless *populneol*,  $C_{16}H_{12}O_3$ , m.p. 116—118°, which is phenolic. Contrary to earlier work (*loc. cit.*), populnetin is a tetrahydroxyflavone,  $C_{15}H_{10}O_6\cdot 0.5H_2O$ , improved m.p. 278—280° (*Ac* derivative, m.p. 242—244°). F. R. G.

**Kanugin, crystalline component of the roots of Pongamia glabra.** S. Rangaswami, J. V. Rao, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, 16, A, 319—322; cf. A., 1942, II, 431).—Light petroleum (b.p. 90—110°) extracts from the root bark a methoxyflavone, *kanugin*,  $C_{16}H_{14}O_4(OMe)_3$ , m.p. 197° (0.05% of dry bark), which gives a red colour with Mg + HCl. A. Li.

**Kanugin. I.** S. Rangaswami and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1943, 17, A, 20—25; cf. preceding abstract).—Oxidation of kanugin (I) by  $KMnO_4$  in  $COMe_2$  yields 4:2:1- $C_6H_3(OMe)(OH)\cdot CO_2H$  (II) and a *OMe-compound*,  $C_{11}H_{14}O_3$  (or  $C_7H_6O_2$ ), m.p. 135—140°, which was hydrolysed (KOH, EtOH) to (probably) (II). Hydrolysis (KOH-EtOH) of (I) in  $H_2$  gives a *OMe-acid*,  $C_8H_8O_4$ , m.p. 145°. Demethylation (HI) of (I) gives a flavonol, *norkanugin*,  $C_{16}H_{12}O_7$ , darkens 290°, the *tri*- (?) -acetate, m.p. 198—199°, sinters 193°, of which with  $Me_2SO_4$  yields a Me ether, m.p. 153°. F. R. G.

**Synthesis of tectorigenin dimethyl ether.** R. L. Shriner and R. W. Stephenson (*J. Amer. Chem. Soc.*, 1942, **64**, 2737—2738).—*p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CN (prep. from PhOMe by aq. CH<sub>2</sub>O—light petroleum—ZnCl<sub>2</sub>—HCl and then aq. NaCN; 29%), b.p. 154—156°/20 mm., with 4 : 5 : 1 : 3-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OH)<sub>2</sub>, ZnCl<sub>2</sub>, and HCl gas in Et<sub>2</sub>O at 0° and then boiling 10% HCl gives 2 : 6-dihydroxy-3 : 4 : 4'-trimethoxydeoxybenzoin (29%), m.p. 116.5°, which with HCO<sub>2</sub>Et—Na at 0° gives tectorigenin Me<sub>2</sub> ether, m.p. 188° (diacetate, m.p. 213°). R. S. C.

**Benzoylation of 5-hydroxy-6-acylcoumarins in presence of pyridine.** N. M. Shah and C. V. Deliwala (*Proc. Indian Acad. Sci.*, 1942, **16**, A, 387—391).—5-Hydroxy-6-acetyl-4-methylcoumarin and BzCl—C<sub>5</sub>H<sub>5</sub>N give, not the *O*-Bz derivative (probably formed initially), but 2'-phenyl-4-methylchromono-7' : 8' : 6 : 5- $\alpha$ -pyrone (I), m.p. 251—252°, also obtained from 5-hydroxy-4-methylcoumarino-6-styryl ketone and SeO<sub>2</sub>—*n*-C<sub>5</sub>H<sub>11</sub>·OH at 170—180°. Unsuccessful attempts were made to remove the 3'-Bz group from 3'-benzoyl-2'-phenyl-4-methylchromono-7' : 8' : 6 : 5- $\alpha$ -pyrone (cf. A., 1938, II, 152). 5-Hydroxy-6-propionyl-4-methylcoumarin (II) (no simple Bz derivative could be obtained) and BzCl—C<sub>5</sub>H<sub>5</sub>N afford 3'-benzoyl-methyl-2'-phenyl-4-methylchromono-7' : 8' : 6 : 5- $\alpha$ -pyrone (III), m.p. 221° (attempts to remove Bz unsuccessful), and the dibenzoyloxy-derivative (IV), m.p. 159—160°, of (II). (III) is also formed by Kostanecki benzoylation (Bz<sub>2</sub>O—NaOBz at 160—170°) of (II). (IV) and HBr—AcOH or conc. H<sub>2</sub>SO<sub>4</sub> give (II). 5-Hydroxy-6-butyryl-4-methylcoumarin reacts in its enol form with BzCl—C<sub>5</sub>H<sub>5</sub>N to give the dibenzoyloxy-derivative, m.p. 168°, whereas Kostanecki benzoylation affords 3'-benzoyl-methyl-2'-phenyl-4-methylchromono-7' : 8' : 6 : 5- $\alpha$ -pyrone, +0.5H<sub>2</sub>O, m.p. 220—221°. The above coumarins with Ac<sub>2</sub>O give only the 5-OAc-derivatives. The action of C<sub>5</sub>H<sub>5</sub>N on resacetophenone dibenzoate does not cause migration of the acid residue, and the above transformations in presence of C<sub>5</sub>H<sub>5</sub>N, with flavone-ring formation, are caused by the presence of the  $\alpha$ -pyrone ring. A. T. P.

**Synthesis of 2-ketocyclohexylsuccinic acid and related substances.**—See A., 1943, II, 165.

**Phenoxthionins.**—See B., 1943, II, 109.

**Hydroxylamine fissions.** I. F. Kröhnke and A. Schulze (*Ber.*, 1942, **75**, [B], 1154—1157).—Treatment of  $\beta$ -piperidino- $\alpha$ -phenylethanol hydrobromide (I) with AcOH—HBr containing a little H<sub>2</sub>O at 150° gives nearly the calc. amount of piperidine (II), ~2% of CH<sub>2</sub>Ph·CHO (III), but no CPhMe. With 90—95% H<sub>3</sub>PO<sub>4</sub> at 100° (I) gives 90—98% of (II) and ~67% of (III) (as semicarbazone), the odour of which only gradually develops. Probable schemes are: OH·CHPh·CH<sub>2</sub>·N: → H<sub>2</sub>PO<sub>3</sub>·O·CHPh·CH<sub>2</sub>·N: → H<sub>2</sub>PO<sub>3</sub>·O·CHPh·CH<sub>2</sub>·OH + NH<sub>3</sub> or OH·CHPh·CH<sub>2</sub>·NC<sub>5</sub>H<sub>10</sub> (IV) → CHPh·CHC<sub>5</sub>H<sub>10</sub> → CHPh·CH·O·PO<sub>3</sub>H<sub>2</sub> + (II) → CHPh·CH·OH → CH<sub>2</sub>Ph·CHO. The last scheme is supported by the production of (III) by dehydration of (IV) by KHSO<sub>4</sub>, ZnCl<sub>2</sub>, or H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. (I) with HBr (*d* 1.49) or conc. HCl gives 65—88% of (II) but only very small amounts of (III).  $\beta$ -Piperidino- $\alpha$ -3 : 4-methylenedioxyphenylethanol hydrobromide and 95% H<sub>3</sub>PO<sub>4</sub> at 60° afford 60% of piperonal. A similar yield is obtained from the  $\alpha$ -*m*-C<sub>6</sub>H<sub>4</sub>Cl compound in 5 hr. at 100°. The  $\alpha$ -*o*-C<sub>6</sub>H<sub>4</sub>Cl substance is much more resistant, giving only 32% of aldehyde after 41 hr. at 100°. H. W.

**Isomerisation during dehydrogenations in the pyridine series.** V. Prelog, A. Komzak, and E. Moor (*Helv. Chim. Acta*, 1942, **25**, 1654—1664).—Condensation of CH<sub>2</sub>Ac·CO<sub>2</sub>H with CH<sub>2</sub>O and NH<sub>2</sub>Me·HCl under "physiological" conditions affords  $\alpha$ - (I), m.p. 132° (picrate, m.p. 172°; 2 : 4-dinitrophenylhydrazones, m.p. 200—200.5°; picrate of Ac derivative, m.p. 175°), and  $\beta$ - (II), m.p. 86° [picrate, m.p. 172°; 2 : 4-dinitrophenylhydrazones hydrochloride, m.p. 235° (decomp.); picrate of Ac derivative, m.p. 155—156°], 4-hydroxy-3-acetyl-1 : 4-dimethylpiperidine (cf. Mannich *et al.*, A., 1926, 522); a base, C<sub>10</sub>H<sub>17</sub>O<sub>2</sub>N [picrate, m.p. 217—220° (decomp.)], is obtained as by-product. (I) and (II) pass by loss of H<sub>2</sub>O into 3-acetyl-1 : 4-dimethyl-1 : 2 : 5 : 6-tetrahydropyridine (III), b.p. 115—116°/14 mm. Hydrogenation (Pd—C in MeOH) of (III) or of its hydrochloride in acid medium gives a mixture of 3-acetyl-1 : 4-dimethylpiperidines (IV), one of which gives a picrate, m.p. 189—190°, a hydrochloride, m.p. 144—147°, and a 2 : 4-dinitrophenylhydrazones, m.p. 147°. (III) or (IV) is hydrogenated (PtO<sub>2</sub> in MeOH) to 1 : 4-dimethyl-3- $\alpha$ -hydroxyethylpiperidine, b.p. 125—135°/27 mm., from which a non-homogeneous picrate, m.p. 137—150°, is derived. 1 : 4-Dimethyl-3- $\alpha$ -hydroxyethyl-1 : 2 : 5 : 6-tetrahydropyridine (IV), m.p. 78—79°, is obtained by the action of Al(OPr<sup>i</sup>)<sub>3</sub> in Pr<sup>i</sup>OH on (III). (III) is dehydrogenated and isomerised by Se at 300°, by Pd—C at 300°, or by Se in boiling xylene to 2 : 3 : 4-trimethylpyridine (VI), b.p. 185° [picrate, m.p. 164°; styphnate, m.p. 169°; picrolonate, m.p. 239°; platinichloride, m.p. 265—266° (decomp.); aurichloride, m.p. 181—182°], oxidised by KMnO<sub>4</sub> to pyridine-2 : 3 : 4-tricarboxylic acid (Me<sub>3</sub> ester, m.p. 101—102°); Me<sub>2</sub>Se is also formed when Se is used. CHMeAc<sub>2</sub> and CN·CH<sub>2</sub>·CO·NH<sub>2</sub> in EtOH containing piperidine afford 5-cyano-6-hydroxy-2 : 3 : 4-trimethylpyridine, m.p. 303°, hydrolysed and decarboxylated to 6-hydroxy-2 : 3 : 4-trimethylpyridine, m.p. 252°; this gives the

corresponding 6-Cl-compound, b.p. 112—115°/15 mm., m.p. 48°, converted (H<sub>2</sub>—Raney Ni) into (VI). (V) is similarly transformed by Se into 4-methyl-3-ethylpyridine. Isomerisation requires the presence of >CO but a double linking is not essential. H. W.

**3-Methoxypyridine [picrate, m.p. 139° (corr.)].**—See A., 1943, III, 294.

**Dihydropyridones.**—See B., 1943, II, 74.

**Nitrogenous compounds in petroleum distillates. XXIV. Isolation and identification of a C<sub>11</sub>H<sub>17</sub>N base from Californian petroleum.** H. L. Lochte, W. W. Crouch, and E. D. Thomas (*J. Amer. Chem. Soc.*, 1942, **64**, 2753—2755; cf. A., 1942, II, 328).—The "non-aromatic" bases (A., 1933, 1305) contain dl-4 : 5-dimethyl-2-sec-butylpyridine (I), b.p. 214°/752 mm. (picrate, m.p. 127—128°), and bases, C<sub>12</sub>H<sub>19</sub>N, b.p. 101°/20 mm., 214°/754 mm. (picrate, m.p. 174°), and C<sub>13</sub>H<sub>21</sub>N (picrate, m.p. 121°). The structure of (I) is proved by prep. of a CHPh<sub>2</sub> derivative, m.p. 143°, failure to condense with Ac<sub>2</sub>O at 210°, and oxidation by O<sub>3</sub>—CCl<sub>4</sub> to *dl*-CHMeEt·CO·NH<sub>2</sub> + Ac<sub>2</sub> and by aq. KMnO<sub>4</sub> at 100° to pyridine-2 : 4 : 5-tricarboxylic acid, anhyd. and +H<sub>2</sub>O m.p. 242—243° (decomp.), stable at 170°. R. S. C.

**Cyanine dyes of the pyridine series. III.** M. Q. Doja and D. Prasad (*J. Indian Chem. Soc.*, 1942, **19**, 377—384; cf. A., 1942, II, 329).—Condensation of *p*-NEt<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO and 2-methylpyridine methiodide by piperidine in boiling abs. EtOH gives 2-*p*-diethylaminostyrylpyridine methiodide, m.p. 241°; the corresponding ethiodide, m.p. 205°, propiodide, m.p. 235°, and butiodide, m.p. 244°, are obtained similarly. In the given order the total range of photographic sensitisation of these dyes is 4250—5650, 4200—5750, 4250—5750, 4200—5800 Å. and the range of uniformly intense sensitisation is 4400—5450, 4350—5500, 4400—5650, and 4350—5750 Å., respectively. On the whole they are better sensitisers than the dyes obtained from *p*-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO (*loc. cit.*). H. W.

**Molecular resonance systems. VIII. Intermediate products of the fission of pyridine. Simple, long-chained polymethine dye.** G. Schwarzenbach and R. Weber (*Helv. Chim. Acta*, 1942, **25**, 1628—1639).—Addition of a solution of CNBr and C<sub>5</sub>H<sub>5</sub>N in Et<sub>2</sub>O to an ethereal suspension of NHEt<sub>2</sub>·HClO<sub>4</sub> yields  $\alpha$ -diethyliminium- $\epsilon$ -pyridiniumglutacondialdehyde diperchlorate (I), [NEt<sub>2</sub>:CH·CH:CH·CH:CH·NC<sub>5</sub>H<sub>5</sub>](ClO<sub>4</sub>)<sub>2</sub>, also obtained from homogeneous solution in EtOH—Et<sub>2</sub>O and purified from accompanying pyridinium perchlorate through the picrate. (I) readily yields NHEt<sub>2</sub> when treated with H<sub>2</sub>O, giving  $\alpha$ -pyridiniumglutacondialdehyde perchlorate (II), [CHO·[CH:CH]<sub>2</sub>·NC<sub>5</sub>H<sub>5</sub>](ClO<sub>4</sub>), m.p. 112—113° (decomp.). (I) and (II) are converted by alkali hydroxide through the red anion [CHO·[CH:CH]<sub>2</sub>·N:CH·[CH:CH]<sub>2</sub>·O]<sup>−</sup> slowly into glutacondialdehyde enolate. 2 mols. of base, probably NHEt<sub>2</sub> + NH<sub>3</sub>, are formed from 1 mol. of (I) or (II); C<sub>5</sub>H<sub>5</sub>N is not produced. (I) and warm NH<sub>2</sub>Ph afford the dianil, [NHPh:CH·[CH:CH]<sub>2</sub>·NHPh]<sup>+</sup>, whilst NHEt<sub>2</sub> gives the perchlorate, [NEt<sub>2</sub>:CH·[CH:CH]<sub>2</sub>·NEt<sub>2</sub>](ClO<sub>4</sub>). Treatment of (I) or (II) with cold alkali followed by acidification of the red solution leads to the dialdehyde (III), CHO·[CH:CH]<sub>2</sub>·N:CH·[CH:CH]<sub>2</sub>·OH; the dark yellow solution of this compound becomes nearly colourless when kept or warmed owing to re-formation of (II). (I), but not (II), and NaOAc give a small proportion of a violet dye, probably [NEt<sub>2</sub>:CH·[CH:CH]<sub>2</sub>·N:CH·[CH:CH]<sub>2</sub>·O], whilst unstable blue-red dyes result from (I) or (II) and piperidine, NHEt<sub>2</sub>, or other aliphatic amine; the colours are well observed when filter-paper impregnated with (I) or (II) is placed in the amine vapour or by working in solution in COMe<sub>2</sub>. (III) gives a dark violet phenylhydrazones which does not crystallise. In dyes of the type (III) a bathochromic effect is produced when 1st, 3rd, 5th, 7th, 9th, or 11th CH is replaced by N but a hypsochromic change when the 2nd, 4th, 6th, 8th, or 10th CH is similarly replaced. H. W.

**Effects of solvents on absorption spectra of dyes.**—See A., 1943, I, 114.

**Derivatives of 2-aminopyridine-5-sulphonamide and of pyrid-2-one-5-sulphonamide.** C. Naegeli, W. Kündig, and H. Suter (*Helv. Chim. Acta*, 1942, **25**, 1485—1498).—The m.p. curves of the substituted amides of C<sub>6</sub>H<sub>4</sub>R·SO<sub>3</sub>H (R = Cl, NH<sub>2</sub>, or OH) are generally similar to those of the corresponding C<sub>5</sub>H<sub>5</sub>N derivatives, showing that the rings retain their general influence on the lattice structure no matter what the substituent may be. With unsubstituted or singly-substituted amides there is no evidence of intramol. salt formation. With derivatives of C<sub>5</sub>H<sub>5</sub>N the association relationships do not appear to be influenced by alkyl substitution. The introduction of NH<sub>2</sub> causes a greater increase of m.p. than does that of OH. With few exceptions the pyridonesulphonic acids and pyridinesulphonamides show a strong fluorescence under ultra-violet light when solid but not in EtOH or H<sub>2</sub>O. The corresponding 2-chloropyridine-5-sulphonamides are converted by aq. NH<sub>3</sub> in presence of a little CuSO<sub>4</sub> in a sealed tube into 2-aminopyridine-5-sulphon-methyl-, m.p. 140—141°, -dimethyl-, m.p. 157—159°, -diethyl-, m.p. 148—149.5°, -*n*-butyl-, m.p. 114—116°, -allyl-, m.p. 136—137°, and -cyclohexyl-amide, m.p. 129—131°, -piperidide, m.p.

160—162°, -morpholide, m.p. 178—180°. 2-Chloropyridine-5-sulphonyl chloride (I) in COMe<sub>2</sub> and glycine in 10% NaOH yield 2-chloropyridine-5-sulphonamidoacetic acid, m.p. 193° (decomp.), converted by conc. NH<sub>3</sub> at 130° into the 2-NH<sub>2</sub>-compound (II), m.p. 226—227° (decomp.). 2-Chloro-, m.p. 193—195°, and 2-amino-, m.p. 250—252° (decomp.), pyridine-5-sulphon-o-amidobenzoic acid are obtained analogously. (I) and NH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Et, HCl in COMe<sub>2</sub>-aq. NaOH afford Et 2-chloropyridine-5-sulphonamidoacetate, m.p. 116—118°, hydrolysed by conc. NH<sub>3</sub> at 145° to (II). 2'-Aminopyridine-5''-sulphon-4-amidobenzenesulphonylsulphanildimethylamide has m.p. 171—172°. The requisite Cl-compounds and boiling aq. NaOH give pyrid-2-one-5-sulphon-2'-pyridylamide, m.p. 268—269°, 2-hydroxypyridine-5-sulphonamidoacetic acid, m.p. 263—264°, and 2-pyridone-5-sulphonanthranilide, m.p. 263° (decomp.). 2'-Chloropyridine-5''-sulphonylsulphanilylsulphanildimethylamide, m.p. 147—149°, from (I) and p-sulphanilylsulphanildimethylamide in C<sub>5</sub>H<sub>5</sub>N, is converted by boiling 10% NaOH into the corresponding pyridone, decomp. 188°. 2-Aminopyridine-5-sulphonic acid and p-NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Cl in aq. NaOH-C<sub>5</sub>H<sub>5</sub>N give 2-p-acetamidobenzenesulphonamidopyridine-5-sulphonic acid, m.p. 326—328°, hydrolysed by boiling 10% NaOH to the p-NH<sub>2</sub>-compound. 2-p-Acetamidobenzenesulphonamidopyridine-5-sulphonamide has m.p. 247° (Ac-free compound, m.p. 227°); the corresponding dimethylamide has m.p. 151—153°. H. W.

Indoles.—See B., 1943, II, 109.

Hofmann type rearrangement in liquid ammonia. H. C. White and F. W. Bergstrom (J. Org. Chem., 1942, 7, 497—507).—2-Phenylquinoline-4-carboxylamide is converted in ~40—50% yield into 4-amino-2-phenylquinoline, m.p. 163.5—164.5°, by reaction with KNH<sub>2</sub> in liquid NH<sub>3</sub>. Almost quant. yields are obtained in the presence of KNO<sub>3</sub> or of Hg. Analogously 2-phenyl-6-methylquinoline-4-carboxylamide gives 4-amino-2-phenyl-6-methylquinoline, m.p. 184—185°, and 2-phenylbenzoquinoline-4-carboxylamide, m.p. 268—269°, yields 4-amino-2-phenylbenzoquinoline, m.p. 162.5—163°. NH<sub>2</sub>Bz, CH<sub>2</sub>Ph·CO·NH<sub>2</sub>, stearamide, and α-phenyl-γ-methyl-α-n-propylvaleramide do not thus give the corresponding amine. o-C<sub>6</sub>H<sub>4</sub>·Bz·CO·NH<sub>2</sub> gives o-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·COPh in 20% yield. 2-β-Naphthyl-, m.p. 250.5—251°, 2-p-tolyl-, and 2-p-anisyl-, m.p. 245—246°, -quinoline-4-carboxylamide react readily with KNH<sub>2</sub> and KNO<sub>3</sub> in liquid NH<sub>3</sub> but without production of well-defined products. It thus appears that a reaction of the above type occurs only if the CO·NH<sub>2</sub> group is activated by C=O or C=N at a favourable position in the mol. 2-p-Xenylquinoline-4-carboxylic acid, m.p. 292—293°, its amide, m.p. 245.5—246°, and 3-phenylbenzoquinoline-4-carboxylamide, m.p. 239—240°, are described incidentally. Direct replacement of CO·NH<sub>2</sub> by NH<sub>2</sub> is very unlikely and it is more probable that R·CO·NH<sub>2</sub> reacts with KNH<sub>2</sub> reversibly to form some of the ion, R·CO·N<sup>-</sup>. This loses 2 electrons to KNO<sub>3</sub> or Hg to give the rearranged product RNCO which excess of KNH<sub>2</sub> transforms into R·NHK and KNCO. The over-all reactions are R·CO·NH<sub>2</sub> + 3KNH<sub>2</sub> + KNO<sub>3</sub> → R·NHK + KNCO + 2NH<sub>3</sub> + KOH + KNO<sub>2</sub> or R·CO·NH<sub>2</sub> + 4KNH<sub>2</sub> + xHg → R·NHK + KNCO + K<sub>2</sub>Hg<sub>x</sub> + 3NH<sub>3</sub>. 2-Phenylquinoline-4-carbimides or 2-phenyl-6-methylquinoline-4-carbimides react with KNH<sub>2</sub> to form the corresponding amine more slowly than this latter is produced in accordance with the above equations from quinoline-4-carboxylamide derivatives. Carbimides are therefore not true intermediates in the reactions or are much more readily hydrolysed by KNH<sub>2</sub> immediately after their formation. Phenyl- and naphthyl-carbimides react with liquid NH<sub>3</sub> at -33° to form monosubstituted carbamides but disubstituted carbamides are also formed in presence of KNH<sub>2</sub>. This can be interpreted as involving the intermediate formation of a salt of a primary amine, e.g., KNHPh, which adds to the carbamide to form a disubstituted carbamide. Accordingly the assumption of the formation of the carbimides (see above) receives some support. 9-Phenyl-9-fluorylamine, KNH<sub>2</sub>, and KNO<sub>3</sub> yield 9-aminophenanthridine (I) by a method related to the Pinck-Hilbert modification of the Stieglitz rearrangement. The expected primary product, 9-phenylphenanthridine, has been converted by KNH<sub>2</sub> into (I). KNH<sub>2</sub>, KNO<sub>3</sub>, and CPh<sub>3</sub>·NH<sub>2</sub> give NH<sub>2</sub>Bz. It is assumed that a Stieglitz type of rearrangement takes place with the formation of CPh<sub>2</sub>·NPh, which is cleaved by KNH<sub>2</sub> to K benzamidine; this is hydrolysed to NH<sub>2</sub>Bz. H. W.

5:5-Dimethylhydantoins containing a NRR substituent. II. H. R. Henze and D. D. Humphreys (J. Amer. Chem. Soc., 1942, 64, 2881; cf. A., 1940, II, 222).—The appropriate NBu<sup>a</sup>R·CH<sub>2</sub>·COMe, KCN, and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in aq. EtOH at 55—60° give the following 5-methyl-5-N-alkyl-N-butylaminomethylhydantoins: alkyl = Me (I), m.p. 137—138°, Et (II), m.p. 136—137°, Pr<sup>a</sup>, m.p. 146—147°, Pr<sup>β</sup>, m.p. 160—162°, Bu<sup>β</sup>, m.p. 177.5—178°, sec.-Bu, m.p. 188—189°, CH<sub>2</sub>Bu<sup>a</sup>, m.p. 165—166°, and CH<sub>2</sub>Bu<sup>β</sup>, m.p. 181.5—182°. (I) and (II) are slightly analgesic in nearly fatal doses. The other products are not hypnotic. R. S. C.

Dihydroglyoxalines.—See B., 1943, II, 76.

Structure of glyoxaline.—See A., 1943, I, 144.

Structures of ketonic complexes of antipyrine.—See A., 1943, I, 116.

Pharmacological studies. XVI. Antipyril ketones. H. P. Kaufmann, L. S. Huang, and H. Bückmann (Ber., 1942, 75, [B], 1236—1247).—Antipyrine (I), antipyrine (II), and P<sub>2</sub>O<sub>5</sub> in CO<sub>2</sub> at 100°/50 atm. yield di-1-phenyl-2:3-dimethylpyrazol-5-on-4-yl ketone [diantipyril ketone], m.p. 246° [hydrochloride, m.p. 184° (decomp.)]; hydriodide, m.p. 229° (decomp.); semicarbazone, m.p. 263°, obtained by heating the reactants in a sealed tube at 150—170°, reduced by Zn dust and AcOH containing Et<sub>2</sub>O at 100° to diantipyrilmethane, m.p. 178—179°. (I), NPhMe<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub> at 120° afford p-dimethylaminophenyl antipyril ketone, m.p. 217°, not identical with the N-antipyril-N-methylaniline, m.p. 147°, derived from antipyril chloride (III) and NPhMe. p-Ethoxyphenyl 4-antipyril ketone, m.p. 194°, is prepared from (I), PhOEt, and P<sub>2</sub>O<sub>5</sub> at 140° and Ph 4-antipyril ketone, m.p. 148°, from (III), C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub>. ZnEt<sub>2</sub> and (III) in boiling Et<sub>2</sub>O or (II) and EtCOCl give 4-antipyril Et ketone, m.p. 146°. 4-Antipyril 2-phenyl-4-quinolyl ketone, m.p. 198°, is obtained from (II), 2-phenylquinoline-4-carboxylic acid, and P<sub>2</sub>O<sub>5</sub> at 150°, and 4-antipyril 6-methoxy-4-quinolyl ketone, m.p. (indef.) 130—132°, from quinic acid, (II), and P<sub>2</sub>O<sub>5</sub> at 110—120° or from quinyl chloride hydrochloride and (II) at 120—130° and subsequently at 120°. (II), CHET<sub>2</sub>·COCl, and AlCl<sub>3</sub> in boiling CS<sub>2</sub> yield 4-antipyril CHET<sub>2</sub> ketone, m.p. 133°. (II) is converted by CH<sub>2</sub>Cl·COCl at 100° into 4-antipyril CH<sub>2</sub>Cl ketone, m.p. 167°, transformed by the usual methods into 4-antipyril CH<sub>2</sub>·NHMe, m.p. 242°, CH<sub>2</sub>·NEt<sub>2</sub>, m.p. 177°, CH<sub>2</sub>·NH·CH<sub>2</sub>Ph, m.p. 222°, CH<sub>2</sub>·NHPh, m.p. 152°, CH<sub>2</sub>·NH·C<sub>6</sub>H<sub>4</sub>·OEt-p, m.p. 185°, CH<sub>2</sub>·CN, m.p. 156°, CH<sub>2</sub>·OH, m.p. 121°, CH<sub>2</sub>·OAc, m.p. 175°, -CH<sub>2</sub>·CO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH-o, m.p. 196° (acetate, m.p. 141°), and antipyril-oxymethyl, m.p. 256°, ketone. (II) and p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·COCl at 130° and then at 100° yield p-nitrophenyl 4-antipyril ketone (V), m.p. 209° (lit. m.p. 165—168°). The corresponding o-nitrophenyl compound has m.p. 172°. Reduction of (V) by SnCl<sub>2</sub> in AcOH saturated with HCl at room temp. or catalytically in EtOH containing Ni or Al<sub>2</sub>O<sub>3</sub> at 160—180°/60 atm. gives p-aminophenyl 4-antipyril ketone (VI), m.p. 260° (Ac derivative, m.p. 216°). o-Aminophenyl 4-antipyril ketone has m.p. 144°. p-Aminophenyl 4-antipyril ketone hydrochloride and KCNO give N-p-antipyrilphenylcarbamide, m.p. 223° (decomp.). N'-Phenyl-N-p-antipyrilphenylcarbamide, m.p. 210°, is derived from (VI) and PhNCO in C<sub>6</sub>H<sub>6</sub> at 100°. H. W.

Pharmacological studies. XV. 1-Phenyl-2:3-dimethylpyrazol-5-one-4-carboxylic acid (antipyrine acid) and its derivatives. H. P. Kaufmann and L. S. Huang [with H. Schmitz and G. Hülten-schmidt] (Ber., 1942, 75, [B], 1214—1236).—Gradual addition of a solution of antipyrine in warm C<sub>6</sub>H<sub>6</sub> to COCl<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> followed by warming the mixture to 50° and cautious addition of dil. NaOH to the cooled solution gives 1-phenyl-2:3-dimethylpyrazol-5-one-4-carboxylic [antipyrine] acid (I), m.p. 213° (decomp.) [Na, K, Ca, Ag, Pb, Cu, and Cu(NH<sub>3</sub>)<sub>4</sub> salts], the constitution of which is established by its conversion by HNO<sub>3</sub>-H<sub>2</sub>O (1:1) at 100° into 4-nitroantipyrine, m.p. 273°, in good yield. Homoantipyrine similarly affords 1-phenyl-3-methyl-2-ethylpyrazol-5-one-4-carboxylic [homoantipyrine] acid, m.p. 178°. (I) is transformed by boiling SOCl<sub>2</sub> into antipyrinecarboxyl chloride (II), m.p. 171—174°, converted by well-cooled, anhyd. HCN into the corresponding cyanide, m.p. 174°, and by MeOH-C<sub>5</sub>H<sub>5</sub>N at 0° into Me antipyrinecarboxylate, m.p. 158°. Analogously prepared are the Et, m.p. 152° (also from the Na salt and EtBr), Bu<sup>β</sup>, m.p. 111°, isoamyl, m.p. 99°, Ph, m.p. 198° [also from (I), P<sub>2</sub>O<sub>5</sub>, and PhOH at 130°], CH<sub>2</sub>Ph, m.p. 126° (from the Na salt and CH<sub>2</sub>PhCl in EtOH), hydroxyquinolyl, m.p. 217°, α-C<sub>10</sub>H<sub>7</sub>, m.p. 175°, and β-C<sub>10</sub>H<sub>7</sub>, m.p. 186°, esters. (II) and warm Cl·[CH<sub>2</sub>]<sub>2</sub>·OH afford β-chloroethyl antipyrinecarboxylate (III), m.p. 144°, obtained also in C<sub>5</sub>H<sub>5</sub>N at room temp. and converted by usual methods into β-cyano-, m.p. 230° (decomp.), β-amino-, m.p. >260° (decomp.), β-methylamino-, m.p. 208°, β-dimethylamino-, m.p. 202° (decomp.), β-diethylamino-, m.p. 135°, β-anilino-, m.p. 242° (decomp.), β-di-phenylamino-, m.p. 134°, β-p-ethoxyanilino-, m.p. 186°, and β-p-carb-ethoxyanilino-, m.p. 175°, -ethyl antipyrinecarboxylate. With CO(NH<sub>2</sub>)<sub>2</sub> and NH<sub>2</sub>·CO<sub>2</sub>Et in C<sub>6</sub>H<sub>6</sub> containing C<sub>5</sub>H<sub>5</sub>N (III) gives β-antipyril-oxymethyl-carbamide, m.p. 130°, and -urethane, m.p. 138°, respectively. (II) in C<sub>5</sub>H<sub>5</sub>N is transformed by o-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Me, salol, and guaiacol respectively into o-carbomethoxyphenyl, m.p. 138°, o-carbo-phenoxyphenyl, m.p. 179°, and o-anisyl, m.p. 163—165°, anti-pyrate. Quinine antipyrate has m.p. 265°. (II) is transformed by lactophenin in C<sub>5</sub>H<sub>5</sub>N into O-antipyril-lactyl-p-phenetidine, m.p. 160°, and 4-O-antipyriloxycetylantipyrine, m.p. 256°, is derived from 4-chloroacetylantipyrine and Na antipyrate in boiling EtOH. (II) and conc. aq. NH<sub>3</sub> yield antipyrinamide [antipyrinecarboxylamide], m.p. 242—243°, also obtained from antipyrine (IV), NH<sub>2</sub>·COCl, and AlCl<sub>3</sub> in boiling CS<sub>2</sub>. It is slowly transformed by P<sub>2</sub>O<sub>5</sub> at 160—170° into antipyrinonitrile, m.p. 224°, also obtained from (IV), CNBr, and AlCl<sub>3</sub> in CS<sub>2</sub>. It does not give a nitroso-reaction and only a weak reaction with FeCl<sub>3</sub>; its basic character is not sharply defined. (II) with the appropriate base yields the corresponding anilide, m.p. 250°, methylamide, m.p. 207°, dimethylamide, m.p. 211°, diethyl-amide, m.p. 107°, benzylamide, m.p. 141°, p-phenetidine, m.p. 186°,

diphenylamide, m.p. 208°,  $\alpha$ -naphthylamide, m.p. 210°,  $\beta$ -naphthylamide, m.p. 230°, *p*-toluidide, m.p. 208°, 2 : 4-dimethylanilide, m.p. 172°, *m*-nitroanilide, m.p. 245°, *p*-nitroanilide, m.p. 230°, piperidide, m.p. 169°, and 2-pyridylamide, m.p. 197°. (II) and *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NHAc in warm C<sub>6</sub>H<sub>5</sub>N afford *N*-acetyl-*N'*-antipyroyl-*p*-phenylenediamine, m.p. 260° (decomp.). Antipyroylphthalimide has m.p. 186° (decomp.). With the requisite base (II) affords NN'-diantipyroylethylenediamine, m.p. 234°, *p*-phenylenediamine, m.p. 370° (decomp.), benzidine, m.p. 304°, and diaminopyridine, m.p. 298°. Antipyroylantipyrylamide has m.p. 246.5°. Antipyrureide, m.p. 251°, gives an *Ac*, m.p. 249°, and an *Et*, m.p. 252°, derivative. Adaline and (II) in warm C<sub>6</sub>H<sub>5</sub> afford *N*-antipyroyl-*N'*-bromodiethylacetylcarbamide, m.p. 182°; the corresponding *N'*- $\alpha$ -bromoisovaleryl compound, m.p. 135°, is obtained from bromural. (II) and NH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Et·HCl in warm C<sub>6</sub>H<sub>5</sub>N give *Et* antipyramidacetate, m.p. 128°. *o*-Antipyramidobenzoic acid, m.p. 228° (*Et*, m.p. 194°, and *Bu*<sup>8</sup>, m.p. 203°, ester), is described. *N*-Antipyroylsulphanilamide, m.p. 261°, and -dimethylamide, m.p. 188°, are obtained from (II) and the requisite sulphanilamide whereas *N*-antipyroylsulphanildiethylamide, m.p. 174°, is derived from (IV) and *p*-diethylaminosulphonylcarbanilyl chloride in C<sub>6</sub>H<sub>5</sub>N. Boiling Ac<sub>2</sub>O transforms (X) into antipyracetic anhydride, m.p. 154°. Antipyracetic  $\alpha$ -ethyl-*n*-butyric anhydride, m.p. 218° (decomp.), benzoic anhydride, m.p. 185°, benzenesulphonic anhydride, m.p. 103°, and *p*-toluenesulphonic anhydride, m.p. 102°, are obtained from (II) and the requisite Na salt or from Na antipyrate and the necessary acid chloride. H. W.

**Pyrimidines.**—See B., 1943, II, 109.

**Derivatives of *o*-3'-acenaphthoylbenzoic acid.**—See A., 1943, II, 165.

**Pyrazoleanthrones.**—See B., 1943, II, 111.

**Dipole moment and structure of *ms*-tetraphenylporphine.**—See A., 1943, I, 117.

**Absorption spectra and structures of cytochrome-*c* and haemoglobin derivatives.**—See A., 1943, I, 114.

**Synthesis of diisooxazole derivatives.** II. C. Musante (*Gazzetta*, 1942, 72, 242—250).—*Et* 5-styrylisooxazole-3-carboxylate (I) in C<sub>6</sub>H<sub>6</sub> with COMe<sub>2</sub> and Na gives the Na salt (II) of 3-acetoacetyl-5-styrylisooxazole, m.p. 131° (*Cu* salt). With NH<sub>2</sub>OH·HCl (III), (II) gives 3'-methyl-5-styryl-3 : 5'-diisooxazole, m.p. 182°, which with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub>, or better CrO<sub>3</sub>-AcOH, gives 3'-methyl-3 : 5'-diisooxazole-5-carboxylic acid, m.p. 227—228° (decomp.) (*Ag* salt; *Me* ester, m.p. 164—165°). In C<sub>6</sub>H<sub>6</sub>, (I) with EtOAc and Na gives *Et* 5-styryl-3-isooxazoloylacetate, m.p. 83—84° (*Cu* salt, decomp. from ~200°), which with 20% H<sub>2</sub>SO<sub>4</sub> at the b.p. gives 3-acetyl-5-styrylisooxazole, m.p. 123° (oxime, m.p. 185—186°; *p*-nitrophenylhydrazone, m.p. 220—221°; semicarbazone, m.p. 234—235°). This in C<sub>6</sub>H<sub>6</sub> with Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and Na, followed by dil. H<sub>2</sub>SO<sub>4</sub>, gives *Et* 5-styryl-3-isooxazoloylpyruvate, m.p. 123—124° [*Cu* salt, m.p. ~220° (decomp.)]. With (III), this gives a diisooxazole. *Et* 3-methylisooxazole-5-carboxylate with EtOAc and Na gives *Et* 3-methyl-5-isooxazoloylacetate, m.p. 52—54° (*Cu* salt, decomp. ~215°), which in dil. H<sub>2</sub>SO<sub>4</sub> gives 5-acetyl-3-methylisooxazole. E. W. W.

**Derivatives of *o*-, *m*-, and *p*-aminobenzamides and related compounds.** N. W. Hirwe and P. Y. Kulkarni (*Proc. Indian Acad. Sci.*, 1942, 16, A, 294—297).—5 : 2 : 1-C<sub>6</sub>H<sub>3</sub>Br<N=CMe<CO<sub>2</sub>O (I) and conc. aq. NH<sub>3</sub> at room temp. and later 0° give 5-bromo-2-acetamidobenzamide, m.p. 194°. 2 : 5 : 1-NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Br·CO<sub>2</sub>H, BzCl, and 10% NaOH at room temp. and later 100° give 5-bromo-2-benzamidobenzoic acid, m.p. 260°, converted by boiling Ac<sub>2</sub>O into 6-bromo-4-keto-2-phenyl-1 : 3-benzoxazine [(I), with Ph for Me], m.p. 193—194°, which with conc. aq. NH<sub>3</sub> at room temp. and later 0° gives 5-bromo-2-benzamidobenzamide, m.p. 211—212°, and thence by warm dil. aq. NH<sub>3</sub> 5-bromo-2-phenyl-4-quinazolone, m.p. >300°. NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Me (prep. from the acid by HCl-MeOH at <10° and then at the b.p.) gives NHAcyl·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Me, which with aq. NH<sub>3</sub> at room temp. gives NHAcyl·C<sub>6</sub>H<sub>4</sub>·CO·NH<sub>2</sub>, converted at > the m.p. into substituted 4-quinazolones. Similarly, *o*-NHBz·C<sub>6</sub>H<sub>4</sub>·CO·NHPh at ~300°, *o*-benzamidobenz-*m*-toluidide [prep. from benzoylanthranyl (II) by *m*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> at 170°], m.p. 220°, at 250°, and *o*-benzamidobenzhydrazide [prep. from (II) by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O], m.p. 176°, at 220° give 2 : 3-diphenyl-, m.p. 186°, 2-phenyl-3-*m*-tolyl-, m.p. 145°, and 3-amino-2-phenyl-, m.p. 184—186°, 4-quinazolone, respectively. *m*-, m.p. 223°, and *p*-Benzamidobenzamide, m.p. 284—285°, *Me p*-acet-, m.p. 114°, and *p*-benzamidobenzoate, m.p. 160°, are described. R. S. C.

**Piperidine and morpholine derivatives.**—See B., 1943, III, 63.

**Chemotherapy. VI. Sulphanilamido-heterocyclic compounds.** G. W. Anderson, H. E. Faith, H. W. Marson, P. S. Winnek, and R. O. Roblin, jun. (*J. Amer. Chem. Soc.*, 1942, 64, 2902—2905; cf. A., 1942, II, 400).—*A*, *B*, *C*, and *D* below denote activity against *E. coli* in a synthetic medium, *A* is <, *B* equal to, that of sulphanilamide, *C* and *D* equal to that of sulpha-pyridine and -thiazole,

respectively. Standard methods yield 2-sulphanilamido-glyoxaline, m.p. 262° (lit. 259°) (*B*), 4-sulphanilamido-1 : 2 : 4-triazole, m.p. 237° (*A*) (N<sup>4</sup>-*Ac* derivative, m.p. 237°), 3-sulphanilamido-4-methylfurazan, m.p. 148—150° (*C*), -5-methyl-1 : 2 : 4-oxadiazole (I), m.p. 211—213° (*C*), and -pyridazine, m.p. 189—190° (*D*), 5-sulphanilamido-3-naphthylisooxazole (II), m.p. 169—170° (*C*), 5-amino-2-sulphanilamido-1 : 3 : 4-thiadiazole, m.p. 259° (*C*), 4-amino-, m.p. 271—272° (*B*), and 4-diethylamino-2-sulphanilamidopyrimidine, m.p. >300° (*A*). 2-Sulphanilamido-oxazole, m.p. 175—176° (*D*), is prepared by way of the *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>NH-derivative, m.p. 175—177°, which is reduced by FeSO<sub>4</sub>-aq. NH<sub>3</sub>. 3-Sulphanilamido-1 : 2 : 4-triazole, m.p. 195—196° (*A*), and 4 : 6-diamino-2-sulphanilamido-1 : 3 : 5-triazine, m.p. 290—295° (*B*), are prepared by way of the *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH-derivatives, which are reduced by Fe dust in AcOH. (I) and (II) are slightly active against *Streptococci* or *Pneumococci* in mice; the other products are inactive. CH<sub>2</sub>Cl·CHCl·OEt and CO(NH<sub>2</sub>)<sub>2</sub> in boiling H<sub>2</sub>O give 2-amino-oxazole, m.p. 96—98°. Adding Ac<sub>2</sub>O and later NaOAc to dihydroxyguanidine hydrobromide in AcOH and treating the product with 40% NaOH gives 3-amino-5-methyl-1 : 2 : 4-oxadiazole, m.p. 117—119°. 3-Aminopyridazine, m.p. 168—170°, is prepared from the 3-Cl-compound by NH<sub>3</sub>-EtOH at 175°, and 2-amino-4-dimethylaminopyrimidine, m.p. 86—88°, from 4-chloro-2-aminopyrimidine by NH<sub>2</sub>Et<sub>2</sub> at 110—120°. M.p. are corr., usually with decomp. for the *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH-compounds. R. S. C.

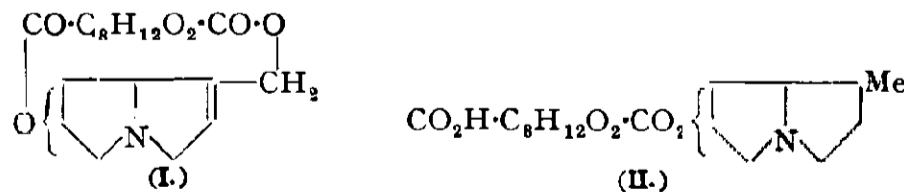
**Sulphanilamide type heterocyclic compounds.**—See B., 1943, III, 63.

**Benzthiazoles.**—See B., 1943, II, 75, 77.

## VII.—ALKALOIDS.

**3 : 2'-Nicotyrine.** Insecticidal properties of azo-derivatives. R. L. Frank, R. W. Holley, and D. M. Wikholm (*J. Amer. Chem. Soc.*, 1942, 64, 2835—2838).—Nicotine and Pd-asbestos in the vapour (41% at 300—325°) or liquid phase (30—35% yield at 230—280°) give 3 : 2'-nicotyrine (I), b.p. 104—107°/1 mm., and fractions, b.p. 210—230°/1 mm. (~30%) and 48—70°/1 mm. By coupling, (I) gives azo-derivatives, C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>·N'·NX, in which X = *p*-C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>Na (II), m.p. >300°, *p*-, m.p. 200—201°, and *m*-C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>, m.p. 156—157°, *p*-C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H, m.p. 245—246° (decomp.), and  $\beta$ -C<sub>10</sub>H<sub>7</sub>, m.p. 148°, which dye wool and protect it considerably from attack by *Attagenus piceus*. SnCl<sub>2</sub>-HCl reduces (II) to 5'-amino-3 : 2'-nicotyrine, m.p. 86—87° [unstable dihydrochloride; stable dipicrate, m.p. 173—174° (decomp.)], unstable in air or hot EtOH, H<sub>2</sub>O, Et<sub>2</sub>O, or CHCl<sub>3</sub>. R. S. C.

**Structure of riddelliine, the alkaloid of *Senecio riddellii*.** I. R. Adams, K. E. Hamlin, jun., C. F. Jelinek, and R. F. Phillips (*J. Amer. Chem. Soc.*, 1942, 64, 2760—2763).—Riddelliine (prep. from *S. riddellii* described; 0—0.7%) (I), C<sub>18</sub>H<sub>23</sub>O<sub>8</sub>N, m.p. 197—198° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>25</sup> -109.5° in CHCl<sub>3</sub> (cf. Manske, A., 1939, II, 232) [hydrochloride, m.p. 225—226° (decomp.; vac.)]. [ $\alpha$ ]<sub>D</sub><sup>25</sup> -80.6° in H<sub>2</sub>O; methiodide, m.p. 260—262° (decomp. from 235°), in boiling aq. Ba(OH)<sub>2</sub> gives retronecine (91%) and riddellic acid (II) (85%), C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>, m.p. (+H<sub>2</sub>O) 62° and (anhyd.) 102—103°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> (anhyd.) -2.65° in EtOH. Hydrogenation (PtO<sub>2</sub>; 2—3 atm.; EtOH) of (II) gives a mixture, but that of its Me<sub>2</sub> ester (prep. by CH<sub>2</sub>N<sub>2</sub>), b.p. 144—145°/1 mm., [ $\alpha$ ]<sub>D</sub><sup>25</sup> -2.84° in EtOH, gives Me<sub>2</sub> dihydro-riddellate, b.p. 146—147°/1 mm., [ $\alpha$ ]<sub>D</sub><sup>25</sup> -15.3° in EtOH. H<sub>2</sub>-Raney Ni at 2—3 atm. reduces (I) in aq. EtOH to tetrahydro-riddelliine (III), m.p. 205°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -9.5° in EtOH, hydrolysed [Ba(OH)<sub>2</sub>] to retronecanol (IV) and (II), but H<sub>2</sub>-PtO<sub>2</sub> in aq. EtOH at 2—3 atm.



gives an amorphous H<sub>8</sub>-compound, hydrolysed to (IV) and an oily acid. (III) has the properties of a NH<sub>2</sub>-acid. Structures are, therefore, as shown. M.p. are corr. R. S. C.

**Alkaloids of fumariaceous plants. XXXV. *Corydalis platycarpa*, Makino.** R. H. F. Manske (*Canad. J. Res.*, 1943, 21, B, 13—16).—The plant contains protopine, *l*-isocorypalmine, isocorydine (identical with luteanine, A., 1939, II, 395), corybulbine, aurotensine, *l*-tetrahydropalmatine, corydaline, bicuculline, *dl*-stylophine, and a neutral compound, C<sub>6</sub>H<sub>9</sub>ON, m.p. 172°. A. L.

**Alkaloids of seeds of *Delphinium elatum*, L.** J. A. Goodson (*J.C.S.*, 1943, 139—141).—The alkaloids of the seeds of *D. elatum* consist mainly of methyl-lycaconitine (I), C<sub>27</sub>H<sub>45</sub>O<sub>10</sub>N<sub>2</sub>, m.p. 128° (sinters at 119°) (not cryst.), [ $\alpha$ ]<sub>D</sub><sup>22</sup> +49.1° in EtOH (purified through the hydriodide, m.p. 201° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>22</sup> +18.5° in *n*-KOH-EtOH), and small quantities of two bases, viz., delpheline, C<sub>22</sub>H<sub>33</sub>O<sub>5</sub>N, m.p. 227° (sinters at 222°), [ $\alpha$ ]<sub>D</sub><sup>15</sup> -25.8° in CHCl<sub>3</sub> [hydrochloride, +H<sub>2</sub>O,

m.p. 219°, with frothing sinters at 215°.  $[\alpha]_D^{25} -42.8^\circ$  in  $H_2O$ ; nitrate, m.p. 191—193°,  $[\alpha]_D^{25} -41.2^\circ$  in  $H_2O$ , and delatine,  $C_{11}H_{13}O_3N$ , m.p. 148° (sinters at 141°) ( $+H_2O$ ),  $[\alpha]_D^{25} +13.5^\circ$  in 0.2N-HCl, or anhyd., m.p. 261—264° (hydrochloride, m.p. 274—277°,  $[\alpha]_D^{18} +13.4^\circ$  in  $H_2O$ ). (I) and  $\alpha$ -NaOH-EtOH afford methylsuccinylanthranilic acid [methyl-lycoctinic acid] (II), m.p. 155° (sinters at 147°),  $[\alpha]_D^{25} -7.0^\circ$  in EtOH, and lycoctonine (III),  $+H_2O$ , m.p. 143° (sinters at 138°),  $[\alpha]_D^{25} +53.2^\circ$  in EtOH, or anhyd., m.p. 126° (sinters at 119° and froths at 143°). (II) is hydrolysed by boiling 10% HCl to l-methylsuccinic acid (IV), m.p. 114° (sinters at 111°), and  $o$ - $NH_2$ - $C_6H_4$ - $CO_2H$ . Hydrolysis of (I) with 10% HCl in a closed vessel at room temp. gives (IV) and anthranoyl-lycoctinine, m.p. 172° (sinters at 168°),  $[\alpha]_D^{25} +32.4^\circ$  in 0.2N-HCl. Hydrolysed by  $\alpha$ -NaOH-EtOH to (III) and  $o$ - $NH_2$ - $C_6H_4$ - $CO_2H$ . (III) is obtainable from the roots of *Aconitum lycoctonum*; thus its presence in these two genera of Ranunculaceae is established. A. T. P.

Alkaloid of *Berberis umbellata*, Wall. III. R. Chatterjee (J. Indian Chem. Soc., 1942, 19, 385—388).—Umbellatine (I) is converted by oxidation with  $KMnO_4$  into hemipinic acid (ethylimide, m.p. 90°) and by fusion with KOH into protocatechuic acid. The 2 OMe groups are *ortho* in the  $C_6H_4$  nucleus of (I) and other groups, such as  $CH_2O_2$  and OH, are not present in this nucleus. H. W.

Alkaloid from *Menispermum canadense*, L. R. H. F. Manske (Canad. J. Res., 1943, 21, B, 17—20).—The subterranean stems and roots contain 2.2% of alkaloid, consisting (? entirely) of dauricine (Kondo *et al.*, A., 1935, 637) (dimethiodide, m.p. 201°,  $[\alpha]_D^{20} -114^\circ$  in  $H_2O$ ), which on exhaustive methylation (dimethiodide of the dimethine base, m.p. 211°) and oxidation ( $KMnO_4$  in  $COMe_3$ ) yields 1:1'-dicarboxy-4-methoxy-, while its *O*-Et ether similarly yields the -4-ethoxy-3:4'-diphenyl ether. A. Li.

Anricularine, a new alkaloid from the roots and stems of *Hedyotis auricularia*. A. N. Ratnagiriswaran and K. Venkatachalam (J. Indian Chem. Soc., 1942, 19, 389—392).—Chemical examination of the root and stems shows the presence of fatty matter yielding stearic and linoleic acids when hydrolysed, a phytosterol, m.p. 141—142° (acetate, m.p. 128—129°), alizarin,  $H_2C_2O_4$ , glucose, auricularine (I,  $C_{42}H_{55}ON_5 \cdot H_2O$ , m.p. 201° (decomp.), becomes brown at 192° [oxalate, becomes brown at 185° and chars without melting at 230°; picrate, m.p. 217—218° (decomp.)], a substance giving a hydriodide, darkens at 195° and chars without melting at 215—220°, and amorphous bases. (I), which differs from hedyotine (Dev *et al.*, A., 1934, 87), is present in very small proportion. H. W.

## VIII.—ORGANO-METALLIC COMPOUNDS.

Relative reactivities of organo-metallic compounds. XLIX. Reactions of group IV  $MR_4$  compounds with silver and copper salts. H. Gilman and L. A. Woods (J. Amer. Chem. Soc., 1943, 65, 435—437).—The fate of R in cleavage of  $MR_4$  by inorg. salts depends on the nature of both reactants. Thus,  $PbPh_4$  with  $AgNO_3$  in EtOH gives 67.5—70.2% of  $Ph_4$  and 74.3—76.8% of  $PbPh_3 \cdot NO_2$ , but with  $Cu(NO_3)_2 \cdot 3H_2O$  in EtOH gives 86.5% of  $C_6H_6$ , a trace of  $Ph_4$ , and 66.8—76% of  $PbPh_3 \cdot NO_2$ .  $SnPh_4$  with  $AgNO_3$  in boiling EtOH gives  $C_6H_6$  (80.6%), and  $Ph_4$  (5.2%).  $PbMe_4$  with  $AgNO_3$  at  $-70^\circ$  gives  $C_2H_6$  (98.3%),  $C_2H_4$  (2.1%),  $PbMe_3$  nitrate (82.7%), and  $CH_4$  (4.0%), and with  $Cu(NO_3)_2 \cdot 3H_2O$  gives  $C_2H_6$  (74.6%),  $PbMe_3 \cdot NO_2$  (71.3% isolated as iodide), and  $CH_4$  (21.1%, formed by hydrolysis of  $CuMe$ ).  $PbEt_4$  with  $AgNO_3$  gives  $C_4H_{10}$  (52.0),  $C_2H_6$  (27.8),  $C_2H_4$  (15.5), and  $PbEt_3Cl$  (72.7%), and with  $Cu(NO_3)_2 \cdot 3H_2O$  gives  $C_4H_{10}$  (52.5),  $C_2H_6$  (26.3),  $C_2H_4$  (16.7), and  $PbEt_3Cl$  (75.7%).  $CuMe$ , formed *in situ* from  $LiMe$  and  $CuI$  in  $Et_2O$  at  $-15^\circ$  (later  $0^\circ$ ), with  $BzCl$  at  $-15^\circ$  gives  $COPhMe$  (56.5%).  $PbMe_4$  in EtOH with  $Cu(NO_3)_2 \cdot 3H_2O$  at  $-70^\circ$  and then  $BzCl$  gives 3% of  $COPhMe$ .  $SiPh_4$  and  $GePh_4$  do not react with  $AgNO_3$  in boiling EtOH. R. S. C.

Bivalent and trivalent rhodium. IV. Polynuclear complexes of rhodium and tin with tertiary arsines. F. P. Dwyer and R. S. Nyholm (J. Proc. Roy. Soc. New South Wales, 1942, 76, 129—132).—( $AsPh_3$ ,  $Me \cdot RhCl_2$ ) with  $SnCl_4$  gives dichlorohexakis(diphenylmethylarsine- $\mu$ -dichlorotinrhodium $^{II}$ - $\mu$ -dichlorodirhodium $^{II}$ - $\mu$ -dichlororhodium $^{II}$ -tin, m.p. 149°, whilst  $RhCl_3$  and  $SnCl_4$  in NaOH with  $AsPh_3$ ,  $Me$  yield (probably) the isomeric dichlorohexakis(diphenylmethylarsine- $\mu$ -dichlororhodium $^{II}$ -tin- $\mu$ -dichloroditin- $\mu$ -dichlorotinrhodium, m.p. 129°.  $RhCl_3$  gives different types of complex with dialkyl- and diaryl-arsines. The following were prepared: dichlorotris- $p$ -tolyl-dimethylarsine- $\mu$ -dichlororhodium $^{III}$ -tin, m.p. 111°, and tetrachlorohexatris(diphenylmethylarsine- $\mu$ -dichlororhodium $^{III}$ -tin- $\mu$ -dichlorotinrhodium $^{III}$ , m.p. 176—178°. These compounds are readily dissociated and the corresponding Br- and I-derivatives could not be isolated. F. R. G.

Serological properties of simple substances. I. Precipitation reactions between antibodies and substances containing two or more haptenic groups. L. Pauling, D. Pressman, D. H. Campbell, C. Ikeda, and M. Ikawa (J. Amer. Chem. Soc., 1942, 64, 2994—3003).— $p$ - $p'$ -Aminobenzeneazophenylarsonic acid is prepared by condensing

$p$ - $NO$ - $C_6H_4$ - $AsO_3H_2$  (I) with  $p$ - $NH_2$ - $C_6H_4$ - $NHAc$  in boiling AcOH or  $p$ - $N_2Cl$ - $C_6H_4$ - $AsO_3H_2$  (II) with  $NHPh \cdot CH_2 \cdot SO_3H$  in 0.3N- $Na_2CO_3$  and hydrolysing the products by aq. alkali.  $p$ - $NH_2$ - $C_6H_4$ - $AsO_3H_2$  (III) or  $p$ - $C_6H_4$ ( $NH_2$ ) $_2$  and (I) give azobenzene-4:4'-diarsonic and  $p$ -benzenedi- $p'$ -azophenylarsonic acid, respectively. Coupling (II) or  $p$ - $N_2Cl$ - $C_6H_4$ - $N_2$ - $C_6H_4$ - $AsO_3H_2$ - $p$  with the appropriate phenol in dil. aq.  $Na_2CO_3$ , sometimes containing 10% of  $C_6H_5N$ , gives *o*-cresol-3:5-, 8-amino-5-sulpho-1-naphthol-2:7-, and 4:4'-dihydroxydiphenyl-3:3'-di- $p$ -azophenylarsonic acid, resorcinol- and phloroglucinol-2:4:6-tri- $p$ -azophenylarsonic acid, 2:4:4'-trihydroxyazobenzene-3:5:3':5'-tetra- $p$ -azophenylarsonic acid, diphenyl-4:4'-di-(4'-azoresorcinol-2'':6''-di- $p$ -azophenylarsonic acid), *o*-cresol-3:5-di- and resorcinol-2:4:6-tri- $p$ - $p'$ -azobenzeneazophenylarsonic acid, diphenyl-4:4'-di-(4'-azoresorcinol-2'':6''- $p$ - $p'$ -azobenzeneazophenylarsonic acid), 4-hydroxy-, 2:4-dihydroxy-, and 4-amino-azobenzene-4'-arsonic acid.  $p'$ -Hydroxybenzeneazo- $p$ -azobenzene- $p'$ -azophenylarsonic acid is similarly prepared in  $NaOAc$ -AcOH. 2:4:4'-Trihydroxyazobenzene and diphenyl-4:4'-di-(2'':4''-dihydroxyazobenzene) are prepared from  $m$ - $C_6H_4$ (OH) $_2$  by  $p$ -OH- $C_6H_4$ - $N_2Cl$  and ( $C_6H_4$ - $N_2Cl$ - $p$ ) $_2$ , respectively, in NaOH.  $p$ - $CO_2Et$ - $NH$ - $C_6H_4$ - $COCl$  and (II) give, after hydrolysis,  $p$ -aminobenz- $p'$ -arsonoanilide. The appropriate acid chloride or anhydride with (III) in alkaline or buffered aq. solution gives carbanilide-4:4'-diarsonic acid, oxal-, succin-, adip-, sebac-, phthal-, isophthal-, and terephthal-dianilide-4:4'-diarsonic acid. For biological results see A., 1943, III, 442. R. S. C.

Preparation of bisarylphosphonic acids. G. M. Kosolapoff (J. Amer. Chem. Soc., 1942, 64, 2982—2983).—Adding  $MgPhBr$  in  $Et_2O$  to  $POCl_3$  in boiling  $Et_2O$  gives, after hydrolysis, 55% of  $Ph_2PO_3H$  and some  $PPh_2O$ .  $p$ - $C_6H_4Cl$ - $MgBr$  gives 51% of di- $p$ -chlorophenylphosphonic acid, m.p. 171—172.5°, and some ( $p$ - $C_6H_4Cl$ ) $_2$ PO. Yields are slightly lower at  $0^\circ$ . Dil. solutions (0.2 mol. per l.) are beneficial. R. S. C.

Mercuriphenyl salts.—See B., 1943, II, 110.

Ionic nature of the Grignard reagent. W. V. Evans and R. Pearson (J. Amer. Chem. Soc., 1942, 64, 2865—2871).—Transference of  $MgBu^aBr$  and  $MgEtBr$  and conductance of  $MgEt_2$  and  $ZnEt_2$  in  $Et_2O$  are determined. Interaction of  $ZnCl_2$  and  $MgEtBr$  in  $Et_2O$  is instantaneous. From these and known facts it is concluded that halogen and alkyl ions are formed from  $MgRX$ , that the cation is small, slow, and co-ordinated with  $Et_2O$ , whereas the anion is large, mobile, and co-ordinated with  $MgRX$ ,  $MgX_2$ , and  $MgR_2$ . R. S. C.

Grignard reactions. XVI. F. C. Whitmore and C. E. Lewis. XVII. Reactions of esters and acid chlorides with Grignard reagents. F. C. Whitmore and W. S. Forster. XVIII. Reactions of magnesium benzyl chloride. F. C. Whitmore and T. K. Sloat (J. Amer. Chem. Soc., 1942, 64, 2964—2966, 2966—2968, 2968—2970; cf. A., 1942, II, 393).—XVI. Substitution on the  $CH_2$  of  $COR \cdot CH_2R'$  decreases the amount of enolisation occurring in presence of  $MgMeI$ ,  $Et$  being more effective than  $Me$ .  $\beta$ -Substitution has much less effect. The following % of enolisation and addition of  $MgMeI$ , respectively, are recorded:  $COMe \cdot CEt$ , 94, 0;  $COMe \cdot CMeEt$ , 84, 0;  $COMe \cdot CMe_2Et$ , 14, 74;  $COMeBu^a$ , 5, 86;  $COMe \cdot CH_2Bu^a$ , 0, 100;  $COBu^a \cdot CEt$ , 85, 0;  $CH_3 \cdot CH \cdot CO \cdot CEt$ , (I) 0, 58;  $CEt \cdot CO_2R$  ( $R = Me$ , b.p. 164—165°/734 mm., or  $Et$ , b.p. 85—87°/30 mm.) 0, 0;  $CMeEt \cdot CO_2Et$  (II, b.p. 73°/35 mm., 25, 45 {apparent enolisation due to that of the ketone formed; cf.  $CMeEt \cdot CO_2Bu^a$  from (II) and  $NaOBu^a \cdot Bu^aOH$ ; b.p. 104—105°/38 mm.} 22, 60);  $CMe_2Et \cdot CO_2Et$ , b.p. 140—141°/744 mm., 0, 100;  $CEt \cdot CO \cdot [CH_2]_2 \cdot OH$ , 58, 27;  $CH_3 \cdot (CO \cdot CEt)_2$  (III) 91.2, 55.2;  $CHMe \cdot (CO \cdot CEt)_2$  (IV) 79.2, 19.2%. The following reactions are recorded:  $EtOAc + MgEtBr \rightarrow CMeEt \cdot OH \rightarrow (+HCl) CMeEt \cdot Cl \rightarrow (Mg; CO_2) CMeEt \cdot CO_2H$ , b.p. 157°/734 mm.  $\rightarrow (SOCl_2) CMeEt \cdot COCl \rightarrow (+MgMeBr) COMe \cdot CMeEt$ , b.p. 77—79°/20 mm. (2:4-dinitrophenylhydrazones, m.p. 73—74°);  $CEt \cdot CO \cdot [CH_2]_2 \cdot OH + CuSO_4 \rightarrow$  (I), b.p. 97°/36 mm., polymerises when kept;  $CEt \cdot COCl + MgMeBr \rightarrow CEt \cdot CH_2 \cdot OH$  (40%), b.p. 96—100°/40 mm. ( $\alpha$ -naphthylurethane, m.p. 131—132°), +  $COBu^a \cdot CEt$ , (43%), b.p. 86—87°/12 mm. (no CO derivatives obtainable);  $CMeEt \cdot COCl + MgMeBr \rightarrow COMe \cdot CMeEt$ , (48%), b.p. 77—79°/20 mm. (2:4-dinitrophenylhydrazones, m.p. 73—74°);  $CMe_2Et \cdot MgCl + MeCHO \rightarrow$  carbinol  $\rightarrow (+CrO_2 \cdot AcOH; <30^\circ) COMe \cdot CMe_2Et$ , b.p. 130°/733 mm. (2:4-dinitrophenylhydrazones, m.p. 112°);  $RCOCl + NaOR' \cdot R'OH \rightarrow RCO \cdot R'$ ; (III) with Na in  $Et_2O$  and then  $MeI$ -dioxan gives (IV) (41%), b.p. 164°/6 mm. (no  $FeCl_3$  colour or Cu salt).

XVII. The following amounts of *sec.* and *tert.* alcohols, respectively, are formed by  $MgRBr$ : (a) from  $Bu^aCOCl$ ,  $R = Et$  60, 26.1,  $Pr^a$  76, 0 [also  $CH_2Bu^a \cdot OH$  (V) 20],  $Pr^a$  53, 0 [also (V) 23],  $Bu^a$  71, 0 [also (V) 28], and  $Bu^b$  26, 0 [also (V) 61]; (b) from  $Bu^aCO_2Me$ ,  $R = Et$  8.6, 76.5,  $Pr^a$  48, 40,  $Pr^b$  0, 44.8,  $Bu^a$  40, 50,  $Bu^b$  25.7, 29.4, (c) from  $CH_2Bu^a \cdot COCl$ ,  $R = Et$  0, 57.6,  $Pr^a$  24.4, 57,  $Pr^b$  26.7, 0 (32.7% of ketone),  $Bu^a$  20.5, 9.9,  $Bu^b$  48.9, 13.8 (20.1% of ketone), (d) from  $CH_2Bu^b \cdot CO_2Me$ ,  $R = Et$  0, 68.5 (5% of ketone),  $Pr^a$  20.4, 61.8 (7% of ketone),  $Pr^b$  16.1, 55.3,  $Bu^a$  0, 71.4 (trace of ketone),  $Bu^b$  9.2, 34.2% (32% of ketone). Non-formation of primary alcohols shows that aldehydes are not intermediates in the reactions. The following are recorded:  $CMe_2Et \cdot COCl$ , b.p. 129.8°/727 mm.;

*βββ-trimethyl-n-γ-hexyl α-naphthylurethane*, m.p. 88—90°; *ββδ-trimethyl-n-γ-hexyl α-naphthyl-*, m.p. 76.5—77.5°, and *phenyl-urethane*, m.p. 58—59°; *ββζ-trimethyl-n-δ-heptyl α-naphthylurethane*, m.p. 99—101°.

XVIII. Adding  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  to  $\text{AcCl}$  at 0° gives 18% of  $\text{o-C}_6\text{H}_4\text{Me}\cdot\text{COMe}$ , but the reverse addition gives only 3% thereof; at 25° 16.5% is obtained. Only the normal products are obtained by adding  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  to  $\text{MeCN}$ ,  $\text{NH}_2\text{Ac}$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{EtOAc}$ ,  $\text{CH}_2\text{PhCl}$ , or  $\text{H}_2\text{O}$  (cf. lit.).  
R. S. C.

## IX.—PROTEINS.

**Iodinated proteins and their action.** I. Abelin (*Helv. Chim. Acta*, 1942, 25, 1421—1432).—Iodination of proteins does not occur homogeneously but leads to mono- and di-iodotyrosine, iodohistidine, iodotryptophan, and products containing thyroxine (I) which yield the latter in pure form after energetic hydrolysis. Although many iodinated proteins resemble the thyroid protein in containing (I) there is a pronounced physiological difference. In contrast to thyroglobulin the intact iodinated proteins are without sp. influence on the glycogen metabolism of the liver or the creatine changes of the heart and striated muscle; they have no action on the activity of heart, lungs, or nervous system. Certain synthetic iodinated proteins cause increased caloric output but in a degree much inferior to that of the thyroproteins. Outside the animal body only (I) can be obtained by chemical means. The prep. of synthetically iodinated proteins with full thyroid activity has not yet been achieved.  
H. W.

**Effect of salts on the formation of protein complexes during heat-denaturation.** A. Kleczkowski (*Biochem. J.*, 1943, 37, 30—36).—The formation of complexes between different proteins undergoing heat-denaturation together occurs in the absence of salts only in mixtures containing  $\text{H}_2\text{O}$ -sol. serum-globulin. The efficiency of salts in promoting the formation of complexes is determined by the valency of the anion on the acid side and of the cation on the alkaline side of the isoelectric point of the protein, ions of higher valency being more effective than those of lower valency.  
H. G. R.

**Fixation of formaldehyde by scleroproteins.** C. T. Baudouy (*Compt. rend.*, 1942, 214, 692—695).—Only those proteins which contain tryptophan and histidine units combine irreversibly with  $\text{CH}_2\text{O}$ . Collagens which do not contain these acids liberate  $\text{CH}_2\text{O}$  quantitatively from the complex by distillation or the action of  $\text{H}_2\text{SO}_4$ . Globin (from horse blood) under the same conditions liberates only 30% of the combined  $\text{CH}_2\text{O}$ .  
P. G. M.

**Tryptophan content of various proteins.** H. S. Milone and E. L. Everitt (*Proc. Soc. Exp. Biol. Med.*, 1942, 51, 82—83).—Tryptophan of a no. of proteins was determined by a short procedure (A., 1939, II, 44) and found to agree with the results already obtained by Jones *et al.* by their longer method (A., 1925, i, 98).  
V. J. W.

**Partial acid hydrolysis of cow-hide gelatin.** A. H. Gordon, A. J. P. Martin, and R. L. M. Synge (*Biochem. J.*, 1943, 37, 92—102).—Cow-hide gelatin is hydrolysed by 10N-HCl at 37°. Electrodialysis at pH 6 effects a separation into basic and neutral fractions of  $\text{NH}_2$ -acids. Analysis of the former suggests that residues of basic  $\text{NH}_2$ -acids are linked to residues of higher  $(\text{NH}_2)_1$ -acids in gelatin. The neutral fraction is acetylated and fractionally chromatographed on  $\text{SiO}_2$  gel; a 4-day hydrolysate yields a glycine-leucine dipeptide, and a 19-day hydrolysate proline-alanine dipeptide, proline-glycine dipeptide, and proline-alanine-glycine tripeptide, in addition to  $(\text{NH}_2)_1$ -acids including *l*-valine. The diketopiperazines isolated by some earlier workers are probably artefacts resulting from the corresponding dipeptides. Evidence is presented to show that acids with longer fatty side-chains, *e.g.*, phenylalanine, leucine, etc., are not linked to one another.  
P. G. M.

**Amino-acid content of gramicidin.** A. H. Gordon, A. J. P. Martin, and R. L. M. Synge (*Biochem. J.*, 1943, 37, 86—92).—Gramicidin (from tyrothricin) is hydrolysed with HCl in aq. AcOH with exclusion of air (cf. Hotchkiss, A., 1942, II, 42). The following  $\text{NH}_2$ -acids have been demonstrated (N as % of total): leucine 20.2, tryptophan 40—45, valine 16.6, alanine 10.1, glycine 5.3—6.6. These vals. are in close agreement with the calc. vals. for a min. mol. containing 30 atoms of N as demanded by a mol. with 24 residues, *i.e.*, 6 leucine, 6 tryptophan, 5 valine, 3 alanine, 2 glycine, and 2 of an unknown hydroxyamino-acid. Gramicidin does not contain serine.  
P. G. M.

**Partition chromatography applied to protein constituents.** A. H. Gordon, A. J. P. Martin, and R. L. M. Synge (*Biochem. J.*, 1943, 37, 79—86).—The theory of partition chromatography in relation to the separation of  $\text{NH}_2$ -acids and peptides is discussed. The prep. of the  $\text{SiO}_2$  gel and the micro-determination of phenylalanine, leucine + isoleucine, valine, methionine, proline, alanine, and tyrosine as their Ac derivatives is described, and the method is applied to hydrolysates of wool and cow-hide gelatin. The val. for phenyl-

alanine-N (as % of total N) in wool hydrolysates is only 0.8%, < half the vals. obtained by earlier workers.  
P. G. M.

**Separation of basic amino-acids from protein hydrolysates.**—See A., 1943, III, 363.

## X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

**Bitter principles of neem oil.** (A) S. Rangaswami. (B) S. Siddiqui (*Current Sci.*, 1942, 11, 367—368, 368).—(A) Polemical. A comparison is drawn between nimbin (I), and nimbinin (II) (Siddiqui, A., 1943, II, 19), and the substances  $(\text{C}_5\text{H}_7\text{O}_2)_n$  and  $(\text{C}_4\text{H}_7\text{O}_2)_n$  isolated from the EtOH extract of neem oil by Murti *et al.* (A., 1942, II, 123).

(B) EtOH extraction of neem oil is too mild and the substances obtained are not the same as (I) and (II).  
F. R. G.

**Quassin. IV. Minor constituent of Jamaican quassia wood.** E. P. Clark (*J. Amer. Chem. Soc.*, 1942, 64, 2883—2884; cf. A., 1938, II, 288).—Mother-liquors (A., 1937, II, 297) from this wood yield 0.015% of a mixture, m.p. 166—167°, partly separated by adsorption into neoquassin and a non-cryst. material.  
R. S. C.

**Action of organic acids on cornstalk lignin.** E. Fisher (*Iowa State Coll. J. Sci.*, 1943, 17, 241—250).—The amount and OMe content of the lignin extracted by aq. org. acids of different concns. is reported. The results show that hydrolysis plays an important part, and that during the extraction with lactic acid fractionation takes place. Aq.  $\text{HCO}_2\text{H}$  containing HCl appears to cause condensation-polymerisation reactions. Anhyd.  $\text{HCO}_2\text{H}$ , AcOH, and  $\text{EtCO}_2\text{H}$  form esters with the lignins they extract. The action of acids on isolated lignin is not the same as on that in the plant. Lactic acid adds  $\text{CO}_2\text{H}$  groups to both natural and isolated lignin; a mechanism for this process is suggested.  
A. Li.

**Toxic principles of poison ivy.**—See A., 1943, III, 447.

## XI.—ANALYSIS.

**Absorption tube tares in carbon and hydrogen micro-determinations.** W. M. MacNevin and J. E. Varner (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 224—225).—The precautions to be observed when using a Pregl-type tube as a control or as a tare in micro-weighings are described.  
J. D. R.

**Micro-determination of hydroxyl content of organic compounds, acetic anhydride-pyridine mixture as reagent.** J. W. Petersen, K. W. Hedberg, and B. E. Christensen (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 225—226).—Free OH is determined by esterification with  $\text{Ac}_2\text{O}-\text{C}_6\text{H}_5\text{N}$  and titrimetric determination of the excess of  $\text{Ac}_2\text{O}$ .  
J. D. R.

**Cerate and periodate oxidimetry. Perchlorato-cerate and periodate ions as oxidants in the determination of organic compounds.** G. F. Smith and F. R. Duke (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 120—122).—The mechanism of the oxidation of aliphatic org. compounds by  $\text{HIO}_4$  using Malaprade's procedure (A., 1928, 867) is discussed. The principles governing the oxidation of aliphatic org. compounds by  $\text{Ce}(\text{ClO}_4)_6$  in presence of 4M- $\text{HClO}_4$  are discussed. Experimental procedure follows that previously given (A., 1941, II, 386) for glycerol. Results of analysis of a series of org. compounds are given. The  $\text{Ce}(\text{ClO}_4)_6$  method is of wider application than the  $\text{HIO}_4$  method; speed of reaction and the no. of oxidation eqivs. are also greater.  
L. S. T.

**Indirect analysis of organic mixtures.**—See A., 1943, III, 447.

**Histochemical reactions for lipin aldehyde and ketones.**—See A., 1943, III, 368.

**$\alpha$ -Naphthol colour test for dihydroxyacetone and hydroxymaleic acid.**—See A., 1943, III, 448.

**Nature of Waser's specific colour reaction for  $\alpha$ -amino-acids.**—See A., 1943, II, 153.

**Adsorption analysis of amino-acids and peptides.**—See A., 1943, I, 151.

**Fluorometric determination of tocopherol.** M. Kofler (*Helv. Chim. Acta*, 1942, 25, 1469—1474).—The substance is dissolved in abs. EtOH and oxidised with conc.  $\text{HNO}_3$ . The resulting solution is shaken with  $\text{H}_2\text{O}$  and light petroleum. The residue from the last solvent is condensed with  $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$  in AcOH and the fluorescence of the resulting phenazine is compared with that produced analogously from a known wt. of tocopherol (I). The method determines essentially free (I); if tocopheryl esters are present the oxidation should be preceded by hydrolysis.  
H. W.

## A., II.—Organic Chemistry

JULY, 1943.

## I.—ALIPHATIC.

Isomerisation of *n*-paraffins.—See B., 1943, II, 142.

Co-ordination of silver ion with unsaturated compounds. II. *cis*- and *trans*- $\Delta^2$ -Pentene. H. J. Lucas, R. S. Moore, and D. Pressman. III. Mixtures of trimethylethylene and cyclohexene. H. J. Lucas, F. W. Billmeyer, jun., and D. Pressman (*J. Amer. Chem. Soc.*, 1943, 65, 227—229, 230—231; cf. A., 1938, II, 224).—II. Distribution consts.  $K_W$  and  $K_D$  for *cis*- (I) and *trans*- $\Delta^2$ -pentene (II) and mixtures thereof between  $CCl_4$  and (i)  $H_2O$  and (ii)  $n$ - $KNO_3$  and argentation consts.  $K_O$  and  $K_E$  are determined. *cis*-Configuration favours solubility in  $H_2O$  and co-ordination. Since (I) and (II) have distinguishable  $K_O$  and  $K_E$ , isomerisation does not occur in the Ag complex. For mixtures of (I) and (II),  $K_W$  and  $K_O$ , but not  $K_D$  and  $K_E$ , agree with the calc. vals.

III. Similar data are recorded for cyclohexene and  $CHMe:CMe_2$ . The lower vals. of  $K_D$  and  $K_E$  for mixtures are due to the effect of one olefine on the solubility of the other in the aq. layer. Mixed olefines may be analysed by means of the above-named consts.

R. S. C.

Polymerisation of pure olefines by phosphoric acid catalyst under atmospheric pressure.—See B., 1943, II, 141.

Structure and ultra-violet spectra of ethylene, butadiene, and their alkyl derivatives.—See A., 1943, I, 176.

Manufacture of butadiene from ethyl alcohol.—See B., 1943, II, 141.

Condensation of aryldiazonium salts and/or hydroxides with secondary nitroalkanes.—See A., 1943, II, 186.

Oil of lavender. I. Lavandulol, a new monoterpene alcohol from oil of lavender. H. Schinz and C. F. Seidel. II. Constitution of lavandulol. H. Schinz and J. P. Bourquin (*Helv. Chim. Acta*, 1942, 25, 1572—1591, 1591—1611).—I. Lavandulol (I), b.p. 94—95°/13 mm.,  $n_D^{20}$  1.46—1.47, is most easily isolated from the esters of oil of lavender, which are hydrolysed and then treated with  $o$ - $C_6H_4(CO)_2O$  to separate linalool from the primary and *sec.* alcohols. From the latter mixture (I) is isolated by fractional distillation and finally purified through the *allophanate* (II), m.p. 117—118°,  $[\alpha]_D^{20}$  -8.5° in MeOH. Isolation of (I) from the free alcohols which contain geraniol (III), nerol, and citronellol is rendered difficult by the presence of much borneol; it may be effected through the *allophanate*, the m.p. of which as thus prepared is 113—115°. In odour (I) closely resembles (III). Their physical properties are closely similar but (I), unlike (III), does not give a compound with  $CaCl_2$  and is not dehydrated by  $o$ - $C_6H_4(CO)_2O$  at 200°. (II) usually has m.p. 117—118°; if large quantities of material are available this can be raised to 119—120° but products of m.p. 110—112° are then also obtained. All specimens give very closely similar (I) on hydrolysis. Alcohols obtained from the specimens of lower m.p. give the same product (*allophanate*, m.p. 119—120°) when warmed with AcOH, probably owing to a transformation of admixed limonene forms into more stable terpinolene forms. (I) gives an *acetate*, b.p. 61—63°/0.3 mm., which resembles linalyl acetate in odour, a 3 : 5-dinitrobenzoate, m.p. 59—60°, which darkens superficially on exposure to light, a non-cryst. phenylurethane, and an *anthraquinone-2-carboxylate*, m.p. 62—63°. Hydrogenation (PtO<sub>2</sub> in EtOAc) of (I) gives a  $H_4$ -derivative, b.p. 93—94°/12 mm.,  $n_D^{20}$  1.4284° (*allophanate*, m.p. 101—102°), which is saturated towards  $C(NO_2)_4$ ; in an individual, unrepeatable experiment with an inefficient catalyst a  $H_2$ -compound was obtained. With  $SOCl_2$  (I) gives a sulphite, hydrolysable to unchanged (I). Attempted degradation of (I) by  $O_3$  or  $KMnO_4$  gives only  $COMe_2$ ,  $CH_2O$ ,  $H_2C_2O_4$ , and an inseparable mixture of more complex fragments. (I) resembles closely the alcohol (IV) obtained by Ruzicka *et al.* (A., 1935, 605) by the condensation of methylheptenone with  $CH_2O$  in presence of  $Ba(OH)_2$ , followed by treatment of the product with  $MgMeI$  and oxidation of the resultant glycol. (IV) gives an *allophanate*, m.p. 113—114°, and a 3 : 5-dinitrobenzoate, m.p. 65—67°, which do not depress the m.p. of the corresponding derivatives of (I). The *anthraquinone-2-carboxylate* of (IV) has m.p. 99—100° and the *allophanate* of the  $H_4$ -derivative of (IV) has m.p. 91—92°. A direct comparison of (I) and (IV) or their derivatives is difficult

since (I) is optically active whereas (IV) is racemic. The identity in structure of (I) and (IV) is established in another manner.

II. Treatment of lavandulyl acetate with  $HBr$ -AcOH at 0° followed by elimination of  $HBr$  by  $C_5H_5N$ , hydrolysis, and purification of the product through the  $H$  phthalate leads to a partly inactive material from which the homogeneous *allophanate* (V), m.p. 139—140°, of *isolavandulol* [ $\beta\zeta$ -dimethyl- $\epsilon$ -hydroxymethyl- $\Delta^2$ -heptadiene] is isolated.  $\beta$ -Methyl- $\epsilon$ -methylene- $\Delta^2$ -hepten- $\zeta$ -one (VI), b.p. 67—68°/11 mm., is obtained in very small yield by condensing methylheptenone (VII) with  $H_2O$ -EtOH- $CH_2O$  containing NaOAc and better from the ketone and paraformaldehyde in boiling  $C_6H_6$ -Et<sub>2</sub>O containing  $NaNH_2$  (0.33 mol.) and  $Na_2SO_4$ ; it is freed from unchanged (VII) by taking advantage of its inability to react with  $NaHSO_3$  and purified through the *semicarbazone*, m.p. 163—165°. The position of its double linkings is established by its absorption spectrum. It is reduced by  $Al(OPr^i)_3$  in  $Pr^iOH$  to  $\zeta$ -methyl- $\gamma$ -methylene- $\Delta^2$ -hepten- $\beta$ -ol, b.p. 84°/13 mm., which closely resembles linalool (VIII) and borneol in odour; it gives an *allophanate*, m.p. 97°, *acetate*, b.p. 81—83°/12 mm., and non-cryst. 3 : 5-dinitrobenzoate. Under defined conditions (VI) is transformed by  $MgMeI$  into  $\beta\zeta$ -dimethyl- $\gamma$ -methylene- $\Delta^2$ -hepten- $\beta$ -ol (IX), b.p. 80—82°/12 mm., which is purified through the borate and characterised as the *phenylurethane*, m.p. 81—82°; it is very similar to (VIII). Allyl isomerisation of (IX) is effected through the bromide, which after treatment with KOAc in  $COMe_2$  and hydrolysis affords an alcohol mixture in which the primary material greatly predominates; after purification through the  $H$  phthalate the products gives an *allophanate*, m.p. 143—144°, which does not depress the m.p. of (V). The incomplete identity of the m.p. is attributed to the presence of terpinolene and limonene forms in differing proportions. (I) is therefore  $\beta\zeta$ -dimethyl- $\epsilon$ -hydroxymethyl- $\Delta^2$ -heptadiene, of which Ruzicka's alcohol is a not quite homogeneous form. *Tetrahydroisolavandulyl allophanate* has m.p. 99—100°, and *isolavandulyl 3 : 5-dinitrobenzoate* has m.p. 74—75°. The differences between  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated terpene alcohols and the occurrence of irregular isoprene chains are discussed.

H. W.

Production of methyl alcohol.—See B., 1943, II, 142.

$\psi$ -Saccharin chloride, reagent for identifying alcohols.—See A., 1943, II, 211.

Purification of aliphatic acids and anhydrides.—See B., 1943, II, 143.

Manufacture of esters of chlorine-containing organic acids.—See B., 1943, II, 143.

Essential unsaturated fatty acids. P. Karrer and H. Koenig (*Helv. Chim. Acta*, 1943, 26, 619—626).—Linoleic acid is converted by boiling  $SOCl_2$  into its *chloride*, b.p. 159°/0.09 mm., and thence by  $CH_2N_2$  in  $Et_2O$  into the corresponding  $CHN_2$  ketone. This is directly treated with  $Ag_2O$  in  $EtOH$  at 60° and the product is hydrolysed to  $\Delta^{14}$ -nonadecadienoic [*homolinoleic*] acid (I), b.p. 177—178°/0.2 mm. (I) is converted by ozonisation in  $CCl_4$  followed by oxidation with  $H_2O_2$  into sebacic acid. Similarly (I) is transformed into the *chloride*, b.p. 173°/0.1 mm.,  $CHN_2$  ketone, and  $\Delta^8\gamma$ -eicosadienoic acid (II), b.p. 198°/0.08 mm. Phytanic or phytadienoic acid, (I), or (II) cannot replace linoleic acid as essential fatty acid and in the organism of the rat there is no appreciable formation of linoleic acid by  $\beta$  oxidation of (II).

H. W.

Jasmine perfumes. II. Synthesis of lactones with jasmone-like structure. L. Ruzicka, F. Lardon, and P. Treadwell (*Helv. Chim. Acta*, 1943, 26, 673—679; cf. A., 1934, 75).—The prep. and purification of  $COMe[CH_2]_3OAc$  from  $CH_2O$  and  $COMe_2$  is very difficult. Hydrogenation (Pd- $CaCO_3$  in EtOAc) of  $CHAc:CH:OBz$  gives  $\gamma$ -keton-butyl benzoate (I) (*semicarbazone*, m.p. 156°; *p*-nitrophenylhydrazone, m.p. 128—128.5°), which gives  $BzOH$  and  $COMe:CH:CH_2$  when distilled in a high vac. but can be purified by mol. distillation. It is hydrolysed with exceptional ease. (I) is transformed by  $n$ - $C_5H_{11}CHBrCO_2Et$  and  $Zn$  in dioxan into  $\beta$ -methyl- $\alpha$ -*n*-amyl- $\Delta^2$ -pentenolactone [*dihydrojasmone lactone*] (II), b.p. 105—108°/0.5 mm., and  $BzOH$ . Similarly (I) and  $Et\alpha\delta$ -tribromo-*n*-heptoate yield  $\beta$ -methyl- $\alpha$ -*n*- $\Delta^2$ -pentenyl- $\Delta^2$ -pentenolactone [*jasmone lactone*] (III), which absorbs 2  $H_2$  (Adams). The odour of (III) resembles that of jasmone and of (II) dihydrojasmone.

H. W.

Electrolysis of mixtures of nitrate with malonic acid, the hydrogen ester of malonic acid, ethyl- and dimethyl-malonic acid, and succinic acid. F. Fichter and W. Steinbuch (*Helv. Chim. Acta*, 1943, 26, 695—704).—Electrolysis of the mixtures gives the nitrates of esters of monobasic OH-acids but the greater part of the material is used in the Kolbe synthesis. Mixtures of  $\text{KNO}_3$  and  $\text{CH}_2(\text{CO}_2\text{K})_2$  give small amounts of  $(\text{CH}_2\cdot\text{O}\cdot\text{NO}_2)_2$  and  $([\text{CH}_2]_2\cdot\text{ONO}_2)_2$ . Under similar conditions  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$  gives  $\text{NO}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ ,  $(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ ,  $\text{EtOAc}$ , and some  $\text{CHO}\cdot\text{CO}_2\text{Et}$ .  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{Et})\cdot\text{CO}_2\text{K}$  yields  $\text{NO}_2\cdot\text{O}\cdot\text{CH}(\text{Et})\cdot\text{CO}_2\text{Et}$  with the two isomeric  $\text{Et}_2$  diethylsuccinates, and  $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ ,  $\text{CH}(\text{Et})(\text{CO}_2\text{Et})_2$ , and possibly  $\text{COEt}\cdot\text{CO}_2\text{Et}$ ,  $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CO}_2\text{K}$  affords  $\text{Et } \alpha$ -hydroxyisobutyrate nitrate, b.p. 89—91°/10 mm. [converted by reductive hydrolysis with  $\text{Ba}(\text{SH})_2$  into  $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$  and by heating with *p*-toluidine at 140° into  $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , m.p. 132—133°, with  $(\text{CMc}_2\cdot\text{CO}_2\text{H})_2$ ,  $\text{CH}_2\cdot\text{CMe}\cdot\text{CO}_2\text{Et}$ , and  $\text{CMe}_2(\text{CO}_2\text{Et})_2$ .  $\text{CO}_2\text{Et}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{K}$  yields  $([\text{CH}_2]_2\cdot\text{CO}_2\text{Et})_2$ ,  $\text{NO}_2\cdot\text{O}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$ , and  $\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ .

H. W.

**Stereochemical studies. XXIII. Optically active dibromosuccinic acids.** B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1941, 14, B, No. 33, 7 pp.).— $\text{CHPhMe}\cdot\text{NH}_2$  is no better than morphine or cinchonine for resolving  $\gamma$ -( $\text{CHBr}\cdot\text{CO}_2\text{H}$ )<sub>2</sub> (I), but is suitable for final optical purification of the stereoisomerides. (I) is shown by its X-ray spectrum to be a racemate and not a *dl*-mixture. Vals. of  $[\alpha]_D^{18}$  for optically active (I) in  $\text{EtOAc}$ ,  $\text{EtOH}$ , and  $\text{H}_2\text{O}$  are given. The decomp. of (I) in neutral solution takes place via a lactone with a of opposite sign, and is inhibited by  $\text{Br}^-$ . M. H. M. A.

**Unsaturated acids and thioacetic acid.** B. Holmberg and E. Schjånberg (*Arkiv Kemi, Min., Geol.*, 1940, 14, A, No. 7, 22 pp.; cf. A., 1939, II, 155).— $\text{AcSH}$  reacts with unsaturated acids, including *cis*- $\text{CO}_2\text{H}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  (I) and  $(\text{CH}\cdot\text{CO})_2\text{O}$  (II), but not *trans*-(I), citraconic anhydride, or aconitic acid, to give (room temp. or 100°) SAc derivatives of saturated acids in good yield, the direction of addition being the same as for  $\text{HCl}$ , except with  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  and (I). The SH-acids (deacetylation with cold aq.  $\text{NaOH}$ ) are oxidised (I-AcOH) to disulphidodiacyds, and their  $\text{CH}_2\text{Ph}$  thioethers with neutral  $\text{H}_2\text{O}_2$  to sulphoxides and thence ( $\text{KMnO}_4$ ) to sulphones. The following are prepared as above:  $\beta$ -acetylthiolpropionic, m.p. 52—54°,  $\beta$ -acetylthiol-, b.p. 129—130°/3 mm.,  $\beta$ -benzylsulphinyll-, m.p. 70—75°, clear at 78° (also from  $\text{CHMeBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ) ( $+ \text{H}_2\text{O}$ , m.p. 66—68°),  $\beta$ -benzylsulphonyll-, m.p. 132—133°,  $\gamma$ -acetylthiol-, b.p. 138.5—139°/3 mm.,  $\gamma$ -thiol-, b.p. 85—87°/0.05 mm. (thiolactone, b.p. 55—56°/3.5 mm., formed on distillation),  $\gamma\gamma'$ -disulphido-di-, m.p. 109—110°, and  $\gamma$ -benzylsulphonyll-butyril-, m.p. 148—149°, acetylthiolsuccinic, m.p. 125—126° [much slower from *trans*- than from *cis*-( $\text{CH}\cdot\text{CO}_2\text{H}$ )<sub>2</sub>] [anhydride, m.p. 71—73°, from (II)],  $\beta$ -acetylthiol- $\beta$ -phenylpropionic, m.p. 95—96°, acetylthiomethylol-, m.p. 90.5—91.5°, and thiomethylol-succinic, m.p. 107.5—108.5° ( $\gamma$ -thiolactone, m.p. 109—110°, on heating), acids. (I) gives slowly the diastereoisomeric  $\alpha$ -acetylthiol- $\beta$ -methylsuccinic acids (III), A, m.p. 151—153°, B (impure), m.p. 108—112° (decomp.), and thence  $\alpha$ -thiol- $\beta$ -methylsuccinic acids (IV), A, m.p. 108—110°, B, m.p. 189—190° (decomp.), and  $\text{CH}_2\text{Ph}$  thioethers, A, m.p. 141—142°, B, m.p. 150—157°.  $\text{Ac}_2\text{O}$  and (IV) B give (III) A.  $\text{SH}\cdot\text{CMe}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (Ac derivative, m.p. 122—123.5°;  $\text{CH}_2\text{Ph}$  thioether, m.p. 153—154.5°) gives with  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$   $\alpha$ -carboxymethylthiol- $\alpha$ -methylsuccinic acid, m.p. 132—133°.

M. H. M. A.

**Configurative relationship between optically active malic and thiomalic acids.**—See A., 1943, I, 154.

**Photometric determination of ascorbic acid.**—See A., 1943, III, 502.

**Production of  $\gamma$ -keto- $\beta$ -methylbutanol and methyl isopropenyl ketone.**—See B., 1943, II, 144.

**Manufacture of polyalkylenepolyamines.**—See B., 1943, II, 144.

**Stereochemistry of labile compounds of trivalent nitrogen.**—See A., 1943, I, 175.

**Structural characteristics of amino-acids.**—See A., 1943, I, 177.

**Occurrence of *d*-glutamic acid in protein of tumours and healthy organs.**—See A., 1943, III, 402.

**Synthesis of peptides by transamination.** R. M. Herbst and D. Shemin (*J. Biol. Chem.*, 1943, 147, 541—547).—Alternate additions of  $\text{N-NaOH}$  and  $\text{ClCO}_2\text{CH}_2\text{Ph}$  to an ice-cold solution of *dl*-alanyl-alanine gives two modifications of *dl*-carbobenzyloxylalanylalanine, m.p. 144.5—145.5° (I) and 168—169° (II) (softens at 165°) respectively, with considerable proportions of material of m.p. 133.5—135° (III), which may be a mol. compound, a solid solution, or a fortuitous mixture of (I) and (II). When an aq. solution of pyruvyl-alanine and *dl*- $\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$  is boiled under  $\text{N}_2$  transamination occurs accompanied by formation of  $\text{CO}_2$  and  $\text{PhCHO}$ . The product is converted by  $\text{ClCO}_2\text{CH}_2\text{Ph}$  into a mixture of (II) and (III). A scheme is suggested for the biological synthesis of peptide chains from non-amino-acid precursors involving two simple reactions, amination and acylation.

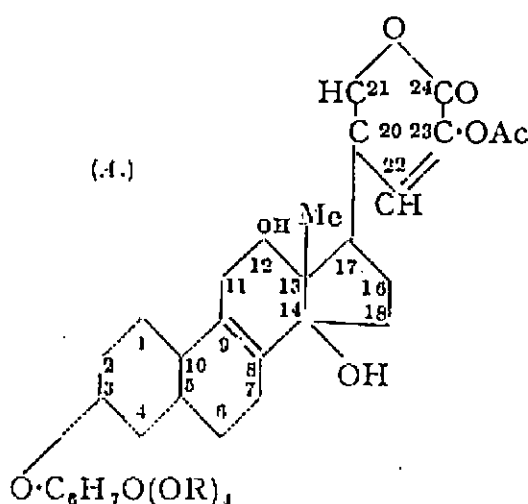
H. W.

**Preparation of urea nitrate.**—See B., 1943, II, 143.

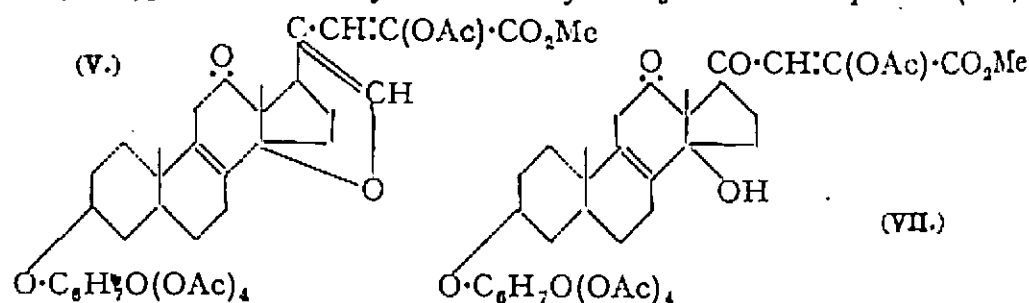
## II.—SUGARS AND GLUCOSIDES.

Raman spectra of sugars.—See A., 1943, I, 176.

**Heart glycosides. XX. Structure of scilliroside.** A. Stoll, J. Renz, and A. Helfenstein (*Helv. Chim. Acta*, 1943, 26, 648—672; cf. A., 1942, II, 218, 279).—The structure (A; R = H) is assigned to scilliroside (I). (I) is oxidised by  $\text{CrO}_3$  or  $\text{Pb}(\text{OAc})_4$  to a substance (II) very freely sol. in  $\text{H}_2\text{O}$  or  $\text{EtOH}$  which could not be



caused to crystallise whereas its tetra-acetate (III) affords *dehydroscilliroside tetra-acetate* (IV) (A; R = Ac. 12-CH-OH to 12-CO), m.p. 228—230°,  $[\alpha]_D^{20}$  -81.8° in  $\text{CHCl}_3$ , -82.5° in  $\text{MeOH}$  (semicarbazone, decomp. 220°), also obtained by acetylation of (II). The absorption curves of (II) and (IV) are very closely similar. (IV) is readily dehydrated by mineral acids in aq.  $\text{EtOH}$  to *anhydrodehydroscilliroside tetra-acetate*, m.p. 228°,  $[\alpha]_D^{20}$  -100° in  $\text{MeOH}$ , the absorption spectrum of which indicates a constitution (A) but with double linkings  $\text{C}_{(8:14)}$  and  $\text{C}_{(9:11)}$ ; the CO group appears to facilitate the formation of a conjugated system. (IV) is converted by treatment with  $\text{NaOH-MeOH}$  followed by dil. acid and then by acetylation into *Me deacetyldehydroisoscilliroside penta-acetate* (V), m.p. 174°,  $[\alpha]_D^{20}$  +55° in  $\text{MeOH}$ . (IV) is hydrogenated ( $\text{PtO}_2$  in  $\text{MeOH}$ ; Pd or Raney Ni does not offer any advantage) to a mixture of neutral isomerides from which a compound (VI),  $\text{C}_{38}\text{H}_{56}\text{O}_{14}$ , m.p. 216—217°,  $[\alpha]_D^{20}$  -52.5° in  $\text{MeOH}$ , is isolated and an acid mixture which yields a substance,  $\text{C}_{38}\text{H}_{58}\text{O}_{14}$ , m.p. 196—198°,  $[\alpha]_D^{20}$  -54.5° in  $\text{MeOH}$ . The corresponding Me ester has m.p. ~155° and does not appear to be homogeneous; it is oxidised to a diketone (*disemicarbazone*,  $\text{C}_{27}\text{H}_{44}\text{O}_4\text{N}_6$ ). Tetrahydrodeacetyldeoxyisoscilliroside is transformed by  $\text{Ac}_2\text{O-C}_6\text{H}_5\text{N}$  into a mixture of *tetra-acetates*, m.p. 240°,  $[\alpha]_D^{20}$  +35° in  $\text{MeOH}$ , and m.p. 219°,  $[\alpha]_D^{20}$  +36° in  $\text{MeOH}$ , the former of which is oxidised by  $\text{Pb}(\text{OAc})_4$  to *tetrahydrodeacetyldeoxydehydroscilliroside tetra-acetate*, m.p. 176—177°, hydrogenated ( $\text{PtO}_2$  in  $\text{MeOH}$ ) to a substance which appears to be identical with (VI). Me deacetylisoscilliroside penta-acetate is resistant towards  $\text{Pb}(\text{OAc})_4$  but is slowly oxidised by  $\text{CrO}_3$  to the compound (VII),



m.p. 192°,  $[\alpha]_D^{20}$  -37.5° in  $\text{MeOH}$  (*disemicarbazone*, decomp. 172°). Me tetrahydrodeacetyldeoxyisoscilliroside (*loc. cit.*, new m.p. 240—242°,  $[\alpha]_D^{20}$  -24.6° in  $\text{MeOH}$ ) is hydrolysed by acid to glucose and a doubly unsaturated acid,  $\text{C}_{24}\text{H}_{34}\text{O}_4$ , m.p. 185° (decomp.) after softening,  $[\alpha]_D^{20}$  -13.5° in  $\text{MeOH}$ , hydrogenated ( $\text{PtO}_2$  or Pd-C) to the saturated acid,  $\text{C}_{24}\text{H}_{38}\text{O}_4$ , m.p. 168°,  $[\alpha]_D^{20}$  +15° in  $\text{MeOH}$ . The presence of a difficultly-reactive, nuclear double linking in (I) is established by the oxidation of (I) by  $\text{BzO}_2\text{H}$  to the corresponding oxide, m.p. 228—230°, softens at 215°,  $[\alpha]_D^{20}$  -34.5° in  $\text{MeOH}$ . The structure of (I) is based on the following considerations. Acid hydrolysis removes from (I) a mol. of glucose which in analogy with the other heart glycosides is supposed to be attached at  $\text{C}_{(3)}$ . The *sec.* nature of OH united to sugar is experimentally established. The aglycon has not been isolated but all the evidence indicates a steroid structure. Absorption spectrum and behaviour towards alcoholic alkali show that (I) like scillaren-A has a doubly unsaturated, six-membered lactone ring; this contains OAc assumed to be  $\alpha$ - to CO. (I) contains a free *sec.* OH which can be oxidised to CO but not acylated; its position at  $\text{C}_{(12)}$  is established. The presence of *tert.* OH, readily removable as  $\text{H}_2\text{O}$ , at  $\text{C}_{(14)}$  is proved. The resistant nuclear double linking in (I) can be hydrogenated after oxidation of OH at  $\text{C}_{(12)}$  or elimination of OH at  $\text{C}_{(14)}$  with production of a second nuclear double linking; this observation and the absorption spectrum of (I) indicate the presence of the linking at  $\text{C}_{(8:9)}$ .

H. W.

**Configuration of starch and its crystalline degradation products.**—See A., 1943, I, 177.

**Non-carbohydrate substances in the cereal starches.**—See A., 1943, III, 446.

## III.—HOMOCYCLIC.

**Highly hindered stilbenes.** R. C. Fuson, J. J. Denton, and C. E. Best (*J. Org. Chem.*, 1943, 8, 64—72).—Three hindered stilbenes

are shown to react with  $H_2$ ,  $KMnO_4$ ,  $O_3$ ,  $BzO_2H$ ,  $Na$ ,  $K-Na$ , and a  $AgOBz-I$  complex normally but frequently much more slowly than do the unhindered stilbenes.  $\alpha\beta$ -Dimesitylethylene (I), m.p. 132.5—133.5°, is obtained by the action of  $MgMeI$ ,  $Mg-MgI_2$ , or  $Mg$  alone on  $C_6H_5Me_3\cdot CHCl_2$ . The yields are nearly the same with the three reagents but the use of Grignard reagent is preferable because it gives a product which is easily purified.  $\alpha\beta$ -Dimesitylethanol (II), m.p. 128—129° (acetate, m.p. 117.5—118°), is obtained by the action of  $H_2$  at 125°/2000 lb. on deoxymesitoin in abs. EtOH containing  $Cu$  chromite or from 2:4:6:1- $C_6H_5Me_3\cdot CHO$  and 2:4:6:1- $C_6H_5Me_3\cdot CH_2\cdot MgCl$  but a tedious separation from  $(CH_2\cdot C_6H_5Me_3)_2$  is required in the latter method. (II) is transformed by  $H_2SO_4-H_2O$  (1:1 by vol.) at 100° into (?) *di-( $\alpha\beta$ -dimesityl)ethyl ether*, m.p. 177—180°, and by  $P_2O_5$  in boiling  $C_6H_6$  or boiling  $Ac_2O$  containing conc.  $HCl$  into (I).  $C_6H_5Me_3\cdot CHO$  and  $CH_2Ph\cdot MgCl$  give  $\beta$ -phenyl- $\alpha$ -mesitylethanol, m.p. 65—66°, also obtained by the action of  $H_2$  at 150°/1550 lb. on  $CH_2Ph$  mesityl ketone in MeOH containing  $Cu$  chromite and converted by  $H_2SO_4-H_2O$  (1:1 by vol.) at 100° into  $\alpha$ -phenyl- $\beta$ -mesitylethylene (III), m.p. 55—56°.  $\alpha$ -Phenyl- $\beta$ -2:4:6-triisopropylphenylethanol is derived from  $C_6H_5Pr^i_3\cdot CHO$  and  $CH_2Ph\cdot MgCl$  and is transformed by  $H_2SO_4-H_2O$  at 100° into  $\alpha$ -phenyl- $\beta$ -triisopropylphenylethylene (IV), m.p. 82.5—83.5°. Treatment of (I) with  $H_2$  at 100° and then at 150°/200 lb. in methylcyclohexane containing Raney  $Ni$  gives  $(CH_2\cdot C_6H_5Me_3)_2$ , m.p. 114—117°; (III) and (IV) are transformed by similar treatment into  $\alpha$ -phenyl- $\beta$ -mesitylethane, m.p. 38—39°, and  $\alpha$ -phenyl- $\beta$ -2:4:6-triisopropylphenylethane, b.p. 155—161°/4 mm., m.p. 33—34°. Ozonisation of (I) followed by treatment of the resulting product with alkaline  $H_2O_2$  gives mesitol (V) and mesitoic acid (VI); analogously (III) yields (V), (VI), and  $BzOH$  and (IV) yields  $BzOH$  and 2:4:6:1- $C_6H_5Pr^i_3\cdot CO_2H$  and  $BzOH$ . (III) and  $BzO_2H$  in  $CHCl_3$  afford  $\alpha$ -phenyl- $\beta$ -mesitylethylene oxide, m.p. 67—68°, reduced by  $HI$  to (III); 1:3:5- $C_6H_3Me_3$  and  $BzO_2H$  in  $CHCl_3$  give (V) in 18.6% yield. Successive treatments of (III) with powdered  $Na$  and solid  $CO_2$  in  $Et_2O$  lead to  $\alpha$ -phenyl- $\beta$ -mesitylsuccinic acid, m.p. 217—219°, converted by boiling  $AcCl$  into the anhydride, m.p. 129—130°.  $\alpha\beta$ -Dimesitylsuccinic acid, m.p. 283—285°, and  $\alpha$ -phenyl- $\beta$ -2:4:6-triisopropylphenylsuccinic acid, m.p. 195—198°, are obtained similarly. Under identical conditions the colour of a solution of  $KMnO_4$  is discharged by stilbene in 1 min., by (III) in 4.5 hr., by (IV) in 30 hr., and by (I) in 60 hr. (I) is converted by the  $I-AgOBz$  complex in boiling  $C_6H_6$  followed by alkaline hydrolysis into hydromesitoin, m.p. 212—213° and 158—159°. (III) appears to give a mixture of the expected glycols. H. W.

**Synthesis of 1-methylnaphthalene.** O. Grummitt and A. C. Buck (*J. Amer. Chem. Soc.*, 1943, 65, 295—296).— $C_{10}H_8$ , paraformaldehyde, and conc.  $H_3PO_4$  in  $AcOH$  at 80—85° give 1- $C_{10}H_7\cdot CH_2Cl$  (70—72%), b.p. 128—133°/5 mm., the Grignard reagent from which gives  $Hg$   $\alpha$ -naphthylmethyl chloride, m.p. 126—128°,  $\alpha$ - $\alpha'$ -naphthylacetophthalide, m.p. 175—177°, and 1- $C_{10}H_7Me$  (80%), b.p. 238—240° (picrate, m.p. 140—141°). R. S. C.

**Nitration of naphthalene.** H. E. Fierz-David and R. Sponagel (*Helv. Chim. Acta*, 1943, 26, 98—111).—Very finely-divided  $C_{10}H_8$  is added gradually to a mixture of 62%  $HNO_3$  and 80%  $H_2SO_4$  at 30—40°, after which the temp. is kept for 6 hr. at 50° and 1 hr. at 60°. The crude product yields 2:4:1-( $NO_2$ ) $_2$  $C_{10}H_5\cdot OH$  (I), m.p. 137° (yield 0.43%), to aq.  $NaOH$ . Distillation of the thus-purified product under 12 mm. gives a mixture (II) of mononitronaphthalenes containing 4.6% of 2- $C_{10}H_7\cdot NO_2$  and a residue in which 1:5- and 1:8- $C_{10}H_6(NO_2)_2$  are identified. Pure 1- $C_{10}H_7\cdot NO_2$ , m.p. 57.8° (block), is best obtained by several crystallisations of (II) from EtOH and from light petroleum. It is distinguished from 2- $C_{10}H_7\cdot NO_2$ , which has an odour of cinnamon, by absence of odour and capability of sublimation in a vac. The nitration of  $C_{10}H_8$  by 95.5%  $HNO_3$  in  $AcOH-Ac_2O$  is described. With ~21%  $HNO_3$  at 95—98° oxidation of  $C_{10}H_8$  is not more marked than with other methods of nitration and the yield of crude nitronaphthalenes is ~94.5%. The detection of 2- $C_{10}H_7\cdot NO_2$  in (II) is best effected by reduction and acetylation followed by the separation of  $\beta$ - $C_{10}H_7\cdot NHAc$  by crystallisation from EtOH. The m.p. diagram of 1- and 2- $C_{10}H_7\cdot NO_2$  is given. Unsuccessful attempts to increase the yield of (I) from  $C_{10}H_8$  by use of dil.  $HNO_3$  in presence of  $NaNO_2$  and by the use of mixed acids with  $NaNO_2$  are described. (I) is primarily formed from  $C_{10}H_8$  and not through 1- $C_{10}H_7\cdot NO_2$ . Nitration of  $C_{10}H_8$  at -60° does not give a trace of 1:3- $C_{10}H_6(NO_2)_2$ , which therefore is unobtainable by direct nitration of  $C_{10}H_8$ . H. W.

**Butylnaphthalenes and their derivatives.** I. 2-tert.-Butylnaphthalene. N. G. Bromby, A. T. Peters, and F. M. Rowe (*J.C.S.*, 1943, 144—146).— $C_{10}H_8$ ,  $Bu^tCl$ , and  $ZnCl_2$  at 70—105° afford 2- $C_{10}H_7\cdot Bu^t$  (I), b.p. 125°/4 mm. (picrate, m.p. 100—101.5°), and two  $C_{10}H_8\cdot Bu^t_2$ , m.p. 146—147°, and 90—95° (picrate, m.p. 157—158°); no 1- $C_{10}H_7\cdot Bu^t$  is isolated. (I) is similarly obtained using  $Bu^tBr$  or by dehydrogenating 2-tert.-butyl-5:6:7:8-tetrahydronaphthalene (II) (from tetrahydronaphthalene,  $Bu^tCl$ , and  $ZnCl_2$ ) with  $S$  at 215—230°.  $p$ - $C_6H_4\cdot Bu^t\cdot CO\cdot [CH_2]_2\cdot CO_2H$  [semicarbazone, m.p. 204—205° (decomp.)] is reduced (Clemmensen) to  $p$ - $C_6H_4\cdot Bu^t\cdot [CH_2]_3\cdot CO_2H$  (amide, m.p. 132—134°), the chloride, b.p. 152—154°/14 mm., of

which with  $AlCl_3$  in light petroleum (b.p. 60—80°) gives 1-*ket*-7-tert.-butyl-1:2:3:4-tetrahydronaphthalene, m.p. 101—102.5° (semicarbazone, m.p. 225—226°). Clemmensen reduction then affords (II), whence (I). (II) is oxidised by aq.  $KMnO_4-Na_2CO_3$  at 95°, followed by  $H_2O_2$ -aq.  $NaOH$  at room temp., to 4-tert.-butylphthalic acid, m.p. 160—161° (anhydride, m.p. 75.5—76.5°). 2-tert.-Butyl-1:4-naphthaquinone, m.p. 76—77° [phenylhydrazone, m.p. 190—191°; *p*-nitrophenylhydrazone, m.p. 264—265° (decomp.)], is obtained from (I) and  $CrO_3$ -50% aq.  $AcOH$  at 65—70°. A. T. P.

**Nuclear alkylated anilines.**—See B., 1943, II, 171.

**Sulphonation of aniline.**—See B., 1943, II, 166.

**Sulphanilamide derivatives.**—See B., 1943, III, 134, 135.

**Sulphilimines derived from sulphanilamide.** C. W. Todd, J. H. Fletcher, and D. S. Tarbell (*J. Amer. Chem. Soc.*, 1943, 65, 350—354).—No product was obtained by heating  $p$ - $NH_2\cdot C_6H_4\cdot SO_2\cdot NH_2$  (I),  $Ph_2SO$  or  $Et_2SO$ , and a dehydrating agent.  $AsPh_3$  and  $AsBu_3$  also do not react. However, the salts,  $p$ - $NHAc\cdot C_6H_4\cdot SO_2\cdot NMX$  [ $M = Na$ ,  $X = Cl$  (II), decomp. 195—205°, or  $Br$ , decomp. 250—260°;  $M = K$ ,  $X = Cl$  (III) (best), decomp. 190—200°, or  $Br$ , decomp. 210—220°] (prep. described), with  $SRR'$  in boiling 60% EtOH or  $H_2O$  at room temp. give 55—85% of  $N^4$ -acetyl-S-dimethyl-, m.p. 141—142° (decomp.), -diethyl-, m.p. 181—182° (decomp.), -di-n-propyl- (IV), m.p. 166—167° (decomp.), -di-n-butyl- (V), m.p. 160—160.5° (decomp.), -di-n-amyl-, m.p. 158.5—160° (decomp.), -diphenyl- (VI), m.p. 204—204.5°, -dibenzyl-, m.p. 192.5—193°, -p-tolyl-S-methyl- (VII), m.p. 180—180.5°, and -di-p-acetamidophenylsulphanilysulphilimine (VIII), m.p. 163.5—164.5° (decomp.),  $p$ - $NHAc\cdot C_6H_4\cdot SO_2\cdot NSRR'$ . In  $HCl$ -dioxan- $H_2O$ , (VI) gives sulphanilyldiphenylsulphilimine (IX), m.p. 183—184°, which is diazotised in quinoline- $H_2SO_4-H_2O$  at <10° and then coupled with  $\beta$ - $C_{10}H_7\cdot OH$  to a product, m.p. 210—211° [(VI) does not thus react], and in conc.  $HCl$  at 100° gives (I) and  $Ph_2SO$ . In 1% aq.  $NaOH-PhMe$ , (V) gives (I) (56%),  $Bu^t_2S$ , and  $Bu^t_2SO$ ; (IV) gives similarly  $Pr^i_2S$ . 2-Acetamidothiazoline (prep. from the amine by  $Ac_2O-C_6H_6$ ), m.p. 194.5—195°, with (II) in aq. dioxan gives the S-oxide, m.p. 199—200°.  $SMe\cdot C(NH)\cdot NH_2\cdot H_2SO_4$ ,  $OEt\cdot CH\cdot C(CO_2Et)_2$ , and  $KOH$  in  $H_2$  at 10° (later 100°) give 6-hydroxy-2-methylthiol-5-carbethoxy-pyrimidine (34%), m.p. 132—133°, which does not condense with (III), but with boiling  $SOCl_2$  gives 6-chloro-2-methylthiol-5-carbethoxy-pyrimidine, m.p. 58—59.5°. 2-Methylthiolquinoline does not condense with (III) but with chloramine-T (X) gives the sulphilimine, m.p. 128—129°.  $R_2S$  and (X) give *p*-toluenesulphonyl-S-di-methyl-, m.p. 154—155°, -n-propyl-, m.p. 110—110.5°, and -n-butyl-sulphilimine, m.p. 77.5—78.5°. Of the sulphilimines, only (VII) is active [ $\ll$  (I)] against *Streptococcus haemolyticus*. (VIII) and (IX) are inactive. (II) and (III) are inferior to (X) as disinfectants. R. S. C.

**Synthesis of sulphanilylamidines.** C. E. Kwartler and P. Lucas (*J. Amer. Chem. Soc.*, 1943, 65, 354—355).— $p$ - $NHAc\cdot C_6H_4\cdot SO_2Cl$  and the appropriate amidine in neutral or slightly alkaline aq.  $COMe_2$  at 0—5° give  $N^4$ -acetylsulphanilyl-acet- (51%), m.p. 241—243°, -propion-, m.p. 192—195°, -butyr-, m.p. 149—151°, -tridec-, m.p. 114—116°, -benz-, m.p. 211—212°, and -phenylacet-amidine, m.p. 193—195°, which in 15—25%  $HCl$ -EtOH at room temp. (not other conditions) give 52—75% of the sulphanilyl-amidines, m.p. 150—152°, 149—151°, 79—82°, 94—95°, 207—209°, and 173—175°, respectively (cf. B.P. 538,822, B., 1941, III, 344; A., 1943, II, 128).  $n$ - $C_{12}H_{25}\cdot CN$  with  $HCl$ - $Et_2O$ -EtOH at 5° gives tridecimino Et ether hydrochloride, m.p. 99—102° (decomp.), which with 9.5%  $NH_3$ -EtOH at room temp. gives tridecamidine hydrochloride, m.p. 135—136°. R. S. C.

**Thermal decomposition of quaternary ammonium phenoxides, with reference to the Claisen rearrangement.** D. S. Tarbell and J. R. Vaughan, jun. (*J. Amer. Chem. Soc.*, 1943, 65, 231—233).— $CH_2\cdot CH\cdot CH_2\cdot NPhMe_2Br$  (I) (prep. from  $CH_2\cdot CH\cdot CH_2Br$  and  $NPhMe_2$  in  $EtOAc$ ), m.p. 125—126°, with  $Ag_2O-H_2O$  gives a solution of the hydroxide, which, when distilled with *m*-2-xylene (II) and  $NaOH$  at 1 atm., gives  $NPhMe_2$  (92%) and 2:6:1- $C_6H_3Me_3\cdot O\cdot CH_2\cdot CH\cdot CH_2$  (III) (77%). Use of  $PhOH$  or *p*-cresol in place of (II) gives  $CH_2\cdot CH\cdot CH_2\cdot OPh$  (IV) (58%) or  $p$ - $C_6H_4Me\cdot O\cdot CH_2\cdot CH\cdot CH_2$  (80%), respectively.  $KOPr^i$ , (I), and (II) in  $Pr^iOH$  give phenyldimethylallylammonium 2:6-dimethylphenoxide,  $+H_2O$ , m.p. 85—87°, and  $+3H_2O$ , m.p. 68—70°, which at 60—85°/2 mm. gives  $NPhMe_2$  (74%) and (III) (69%). Treating (I) in  $H_2O$  with  $AgOPh$ , filtering, and distilling gives  $NPhMe_2$  (81%) and (IV) (59%). It is concluded that the rearrangement of phenol allyl ethers does not occur by cleavage into allyl and phenoxide ions. R. S. C.

**Condensation of aryldiazonium salts and/or hydroxides with secondary nitroalkanes.** C. F. Feasley [with E. F. Degering] (*J. Org. Chem.*, 1943, 8, 12—16).— $ArN_2Cl$  is neutralised with  $NaOH$  and immediately treated with a solution of the sec.  $NO_2$ -alkane in  $NaOH$ ; as soon as the reaction is complete the product should be isolated from the ice-cold solution but in the case of alkali-sol. products

sufficient time must be allowed for the coupling before addition of acids. In stability of the chromophoric azo-linking and ease of purification, these products are superior to those derived from the primary NO<sub>2</sub>-alkanes. If the original amine contains acidic auxochromic groups, the condensation product dyes silk and wool directly; coupling may be made on the fibre. The following are described:  $\beta$ -nitro- $\beta$ -benzeneazo-, b.p. 98.0°/7 mm.,  $\beta$ -o-, m.p. 56.9°, and  $\beta$ -m-, m.p. 71.2—72.2°, -nitrobenzeneazo-,  $\beta$ -4-nitro-o-tolueneazo-, m.p. 70.1°,  $\beta$ -p-acetamidobenzeneazo-, m.p. 125.3—125.8°,  $\beta$ -p-chlorobenzeneazo-, m.p. 67.8°;  $\beta$ -p-bromobenzeneazo-, m.p. 90—91°,  $\beta$ -2:5-dichlorobenzeneazo-, m.p. 57—58°,  $\beta$ -2:4:6-tribromobenzeneazo-, m.p. 58.1°,  $\beta$ -p-tolueneazo-, m.p. 20±1°;  $\beta$ -o-, m.p. 93.2—93.6°, and  $\beta$ -p-carboxybenzeneazo-, m.p. 167—169°, and  $\beta$ -2-naphthaleneazo-propane, m.p. 67°;  $\beta$ -nitro- $\beta$ -m-nitrobenzeneazo-, m.p. 63.3—63.7°,  $\beta$ -4-nitro-o-tolueneazo-, m.p. 48.9°,  $\beta$ -2:5-dichlorobenzeneazo-, m.p. 40—40.3°,  $\beta$ -2:4:6-tribromobenzeneazo-, m.p. 57.4—58°, and  $\beta$ -p-carboxybenzeneazo-butane, m.p. 129—130°.  $\beta$ -Nitro- $\beta$ -phenyl-1:4-phenylenedisazo-propane, m.p. 107—108°, and -butane, m.p. 80.9—81.4°, are described. pp'-Di- $\beta$ -( $\beta$ -nitropropaneazo)di-phenyl has m.p. 162—163.6°. H. W.

**Products of the action of azobenzene-*p*-carboxyl chloride on  $\alpha$ -aminocarboxylic acids and their esters.** P. Karrer, R. Keller, and G. Szönyl (*Helv. Chim. Acta*, 1943, 26, 38—50).—Attempts are described to obtain *N*-acyl derivatives of NH<sub>2</sub>-acids suitable for chromatographic separations. Agitation of *p*-PhN<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·COCl (I) in Et<sub>2</sub>O with *L*-valine in 2*N*-NaOH at room temp. affords 2-*p*-benzeneazophenyl-4-isopropylloxazol-5-one [*N*-*p*-benzeneazobenzoylvaline lactone] (II), m.p. 115°, (which gives dark violet alkali salts), *l*- (III), m.p. 157—159°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -44.85° in EtOH, and *r*-, m.p. 229—230°, -*N*-*p*-benzeneazobenzoylvaline, the latter arising from the hydrolysis of (II). Under similar conditions (I) and *L*-leucine yield 2-*p*-benzeneazophenyl-4-isobutylloxazol-5-one, m.p. 147°, and *r*-*N*-*p*-benzeneazobenzoyl-leucine (IV), m.p. 173°. Glycine yields *N*-*p*-benzeneazobenzoylglycine (V), m.p. 225°, apparently without the corresponding lactone. *l*(+)-*N*-*p*-Benzeneazobenzoylalanine (VI), m.p. 220°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +55.07° in COMe<sub>2</sub>, but no lactone is derived from *l*(+)-alanine. The *Me* esters of (III), m.p. 138°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -38.4° in COMe<sub>2</sub>, (IV), m.p. 133°, (V), m.p. 118°, and (VI), m.p. 148°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +38.4° in COMe<sub>2</sub>, are obtained by means of CH<sub>2</sub>N<sub>2</sub>. Gradual addition of (I) to the appropriate NH<sub>2</sub>-acid ester hydrochloride in C<sub>6</sub>H<sub>5</sub>N at 40—60° leads to the *Me* esters of *N*-*p*-benzeneazobenzoyl-*L*-leucine (VII), m.p. 104°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +22.6° in COMe<sub>2</sub>, -*L*-glutamic acid, m.p. 126—128°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -11.6° in COMe<sub>2</sub>, -*L*-phenylalanine, m.p. 145—146°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -99.2° in COMe<sub>2</sub>, -*L*-aspartic acid, m.p. 148—150°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -17.3° in COMe<sub>2</sub>, -*L*-methionine, m.p. 118—119°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -27.32° in COMe<sub>2</sub>, and -*L*-proline, m.p. 125—126°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -36.27° in COMe<sub>2</sub>. The chromatographic separation of mixtures of the *Me* esters of (V), (VI), and (III) with (VII) on basic Zn carbonate is described; Ca(OH)<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are less suitable. H. W.

**Nuclear methylation of  $\alpha$ -naphthol. A correction.** J. W. Cornforth, (Mrs.) R. H. Cornforth, and (Sir) R. Robinson (*J. C. S.*, 1943, 168; cf. A., 1943, II, 28).—The substance obtained from "4-piperidinomethyl-1-naphthol" (I) and NaOMe-MeOH is not 4:1-C<sub>10</sub>H<sub>7</sub>Me·OH, but 2:4-dimethyl-1-naphthol, m.p. 84—85° (picrate, m.p. 143—144°). That (I) is actually the 2:1-derivative (cf. Feldman *et al.*, A., 1942, II, 205) is confirmed by hydrogenation (Cu chromite in EtOH at 165°/100 atm.) to 2:1-C<sub>10</sub>H<sub>6</sub>Me·OH (picrate, m.p. 133—134°). A. T. P.

**Colour reactions for stilbæstrol.**—See A., 1943, II, 212.

**Mixed  $\beta$ -naphthyl thioethers.** F. E. Ray and G. L. Bowden, jun. (*J. Amer. Chem. Soc.*, 1943, 65, 297).— $\beta$ -C<sub>10</sub>H<sub>7</sub>·SH, AlkBr, and NaOEt in EtOH give  $\beta$ -C<sub>10</sub>H<sub>7</sub>·n-hexyl, b.p. 160°/20 mm., and n-heptyl sulphide, m.p. 34°. *p*-C<sub>6</sub>H<sub>4</sub>Ph·CHPhCl and  $\beta$ -C<sub>10</sub>H<sub>7</sub>·SH in C<sub>6</sub>H<sub>6</sub> give  $\beta$ -C<sub>10</sub>H<sub>7</sub>·phenyl-*p*-xenylylmethyl sulphide, m.p. 155° (sulphoxide, m.p. 220°), which with Me<sub>2</sub>SO<sub>4</sub> gives *p*-C<sub>6</sub>H<sub>4</sub>Ph·C·Ph·S<sup>+</sup>Me·C<sub>10</sub>H<sub>7</sub>· $\beta$ . whence it is regenerated by H<sub>2</sub>O. R. S. C.

**Aryl hydroxyalkyl ethers.**—See B., 1943, II, 172.

**Ethers of duroquinol.**—See B., 1943, III, 135.

**Synthesis of *cis*- and *trans*-3- $\Delta^0$ -pentadecenylveratrole, a dihydro-derivative of urushiol dimethyl ether.** D. Wasserman and C. R. Dawson (*J. Org. Chem.*, 1943, 8, 73—82).—Et<sub>2</sub> adipate is reduced (H<sub>2</sub> at 255°/1750 lb. in presence of Cu-Cr oxide) to [CH<sub>2</sub>]<sub>6</sub>(OH)<sub>2</sub>, b.p. 128—130°/6 mm. (yield 84%), converted by the successive actions of Na and CH<sub>2</sub>PhCl in xylene at 120—130° and then at 120° into  $\zeta$ -benzyloxyhexanol, b.p. 154°/2.5 mm. This with SOCl<sub>2</sub> in NPhMe<sub>2</sub> at 30—45° gives  $\zeta$ -benzyloxy-n-hexyl chloride, b.p. 138°/1 mm., the Mg derivative of which with 2:3:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO affords the expected *sec.* alcohol, converted (without purification) by KHSO<sub>4</sub> at 210° into H<sub>2</sub>O and 3- $\eta$ -benzyloxy- $\Delta^0$ -heptenylveratrole, b.p. 229°/1 mm.; this is reduced (H<sub>2</sub> at 2—3 atm., Pd-black, AcOH) to 3- $\eta$ -hydroxyheptylveratrole, b.p. 169°/2.7 mm. (together with a little *ap.*-dihydroxydodecane, m.p. 82—82.5°), which with HBr at 140—150° followed by re-methylation yields 3- $\eta$ -bromoheptylveratrole, b.p. 174°/1 mm. With CH<sub>2</sub>CN in liquid NH<sub>3</sub> this affords 3- $\Delta^0$ -noninenylveratrole, b.p. 146°/2 mm., transformed by NaNH<sub>2</sub> and *n*-C<sub>6</sub>H<sub>13</sub>Br in liquid

NH<sub>3</sub>-light petroleum into 3- $\Delta^0$ -pentadecenylveratrole (I), b.p. 192°/1.4 mm. (I) is hydrogenated (Raney Ni in 95% EtOH at 31°) to *cis*-3- $\Delta^0$ -pentadecenylveratrole (II), b.p. 198°/2 mm., but is reduced by NaNH<sub>2</sub> in liquid NH<sub>3</sub> to the *trans*-isomeride (III), b.p. 212°/3.2 mm., of (II). Complete hydrogenation (Raney Ni) gives 3-pentadecylveratrole [tetrahydrourushiol Me<sub>2</sub> ether], m.p. 36.8—37°. (III) is oxidised by powdered KMnO<sub>4</sub> in COMe<sub>2</sub> to *n*-C<sub>6</sub>H<sub>13</sub>·CO<sub>2</sub>H and 2:3:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>H. 2:3:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO is reduced (Clemmensen) to 2:3-dimethoxytoluene, b.p. 103°/22.5 mm. H. W.

**2:4-Dinitro-5-arylamino-phenols.**—See B., 1943, II, 172.

**4-Nitro-3-ethoxytoluene-6-sulphonic acid.** C. Buchanan, J. D. Loudon, and J. Robertson (*J. C. S.*, 1943, 168—169).—*m*-C<sub>6</sub>H<sub>4</sub>Me·OEt (I) and conc. H<sub>2</sub>SO<sub>4</sub> at <30° give 3:1:6-OEt·C<sub>6</sub>H<sub>3</sub>Me·SO<sub>3</sub>H (II) (*p*-toluidine salt, m.p. 100—120°; chloride, b.p. 176—177°/10 mm.; amide, new m.p. 113—114°). (I) and conc. H<sub>2</sub>SO<sub>4</sub> at 30—35° for 12 hr. followed by HNO<sub>3</sub> (*d* 1.42)—H<sub>2</sub>SO<sub>4</sub> at 15—18°, then at room temp., yield 4:1:3:6-NO<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>Me(OEt)·SO<sub>3</sub>H (III) (*p*-toluidine salt, m.p. 232—233°; chloride, m.p. 110—111°) and some 2-NO<sub>2</sub>-isomeride (gelatinous *p*-toluidine salt; chloride, m.p. 97°). (III) is also formed from 4:1:3-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me·OEt and ClSO<sub>3</sub>H at 20°. When HNO<sub>3</sub> is added to (I)—H<sub>2</sub>SO<sub>4</sub> at 10—15°, then at 15—20°, 6:1:3-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me·OEt is obtained. 2:4:1:3:6-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>HMe(OEt)·SO<sub>3</sub>H (*p*-toluidine salt, m.p. 225—227°; chloride, m.p. 104°) is obtained from (II) (Na salt) and HNO<sub>3</sub> (*d* 1.5)—H<sub>2</sub>SO<sub>4</sub> at <30°, or [with some (III) and 4:6:1:3-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Me·OEt] from (II) and HNO<sub>3</sub> (*d* 1.5). (III) (Na salt) and aq. NaOCl-NaOH at 50—55° afford a trace of stilbene derivative [*p*-toluidine salt, m.p. ~285° (decomp.)]; sulphonyl chloride, C<sub>18</sub>H<sub>16</sub>O<sub>10</sub>N<sub>2</sub>Cl<sub>2</sub>S<sub>2</sub>, m.p. 212—215°, whereas at 85°, then at room temp., similar treatment yields a substance (*p*-toluidine salt, C<sub>18</sub>H<sub>16</sub>O<sub>12</sub>N<sub>2</sub>S<sub>2</sub>·2C<sub>7</sub>H<sub>9</sub>N, decomp. 310—311°), converted by Fe-HCl at 100° into a substance, C<sub>18</sub>H<sub>22</sub>O<sub>8</sub>N<sub>2</sub>S<sub>2</sub>·2H<sub>2</sub>O, m.p. >350°. A. T. P.

**1-Nitro-1- $\alpha$ -hydroxyethylcyclohexane.**—See B., 1943, II, 172.

**isoPhorone and its derivatives.** A. A. Dodge and E. Kremers (*J. Amer. Pharm. Assoc.*, 1942, 31, 527—529).—isoPhorone (I) (oxime, m.p. 77—78°; semicarbazone, m.p. 190—191°) is hydrogenated (Pt; 2 H<sub>2</sub> absorbed) to 3:3:5-trimethylcyclohexanol, m.p. 58.5—59° (3:5-dinitrobenzoate, m.p. 98.5—99°; acetate, an oil), dehydrated to an oil from which is separated (?) 1:3:3-trimethylcyclohexene, b.p. 139—141°. The liquid (3:5-dinitrobenzoate, m.p. 61.5—63°) and cryst. "isophoronyl alcohol," m.p. 38° (3:5-dinitrobenzoate, m.p. 71.5—72.5°), are probably *cis*- and *trans*-dihydroisophorol. F. O. H.

**Phenol-formaldehyde resins. II. Condensation of dihydroxy-benzenes with formaldehyde.** H. von Euler, E. Adler, and G. J. Gie (*Arkiv Kemi, Min., Geol.*, 1940, 14, B, No. 9, 7 pp.; cf. B., 1942, II, 25).—Quinol (I) (1 mol.), CH<sub>2</sub>O (2 mols.), and 10% NaOH (2 mols.) give (36 hr.; room temp.) exclusively 2:5-di(hydroxymethyl)quinol (II), m.p. (rapid heating) 190—191° (decomp.) [with Me<sub>2</sub>SO<sub>4</sub> gives the 1:4-Me<sub>2</sub> ether, m.p. 163—164°, and thence (KMnO<sub>4</sub>-NaOH) 2:5:1:4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub>, which yields (FeCl<sub>3</sub>) the quinone, m.p. 138°, and the quinhydrone, m.p. 160° (decomp.), deep blue. With 4 mols. of CH<sub>2</sub>O and 4% NaOH (1 mol.) (I) (1 mol.) gives (72 hr.; room temp.) tetra(hydroxymethyl)quinol (III), m.p. (rapid heating) 212—213° (decomp.). On slow heating (II) and (III) give dark resols without melting. *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> (1 mol.), CH<sub>2</sub>O (2 mols.), and 10% NaOH (2 mols.) give (36 hr.; room temp.) exclusively a di(hydroxymethyl)pyrocatechol (IV), m.p. 116—117° (Me<sub>2</sub> ether, m.p. 92°). (II) and (IV), but not (III), are converted into amorphous insol. products very rapidly by hot dil. acids, probably by condensation involving elimination of H<sub>2</sub>O between nuclear H of one mol. and CH<sub>2</sub>·OH of a second mol. etc. M. H. M. A.

**Phenol-formaldehyde resins. VIII. Mechanism of the hardening of resols; formation of dibenzyl ethers.** H. von Euler, E. Adler, and J. O. Cedwall (*Arkiv Kemi, Min., Geol.*, 1941, 14, A, No. 14, 20 pp.).—Evidence is adduced in favour of the view that the action of heat on *o*-hydroxybenzyl alcohols consists mainly in the formation of di-*o*-hydroxybenzyl ethers with minor quantities of diphenylmethanes. 2:3:5:1-OH·C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·CH<sub>2</sub>·OH (I) at 140° gives an alkali-insol. substance (II), m.p. 200°, di-2-hydroxy-3:5-dimethylbenzyl ether (III), m.p. 99—100°, di-(2-hydroxy-3:5-dimethylphenyl)methane (IV), m.p. 146°, and a non-cryst. residue (34% of the original material) from which NaOH separates an alkali-insol. portion (V). (II) does not give a colour with FeCl<sub>3</sub>, is extraordinarily stable towards acids and bases, cannot be acetylated or methylated, and does not react with ketonic reagents. It is identical with the "polymeric xylo-*o*-methylenequinone" of Fries *et al.* (A., 1907, i, 603) but is probably C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub><O·CH<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·O·CH<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·O·CH<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·CH<sub>2</sub>·. The yield is 4—8% at 140° increasing to 30% at 180°. (III) gives an intense violet colour with FeCl<sub>3</sub>, yields a dibenzoate (VI), m.p. 108—108.5°, and reacts vigorously with CH<sub>2</sub>N<sub>2</sub> giving a Me<sub>1</sub> ether (VII), b.p. 155—160°/0.1 mm., which is insol. in NaOH but contains OH since it yields a *p*-nitrobenzoate, m.p. 120—121°. (VII) is

oxidised by  $\text{KMnO}_4$  to 2-methoxy-3:5-dimethylbenzoic acid, m.p. 97—98°. Treatment of (III) or (VII) with  $\text{Me}_2\text{SO}_4$ -2N-NaOH-MeOH gives the  $\text{Me}_2$  ether (VIII), m.p. 73—74°. The constitution of (III) is further established by its production when the *p*-toluenesulphonate of (I) is heated at 195—200° and the product hydrolysed. (I) or (III) and HBr in light petroleum at room temp. give 2-hydroxy-3:5-dimethylbenzyl bromide (IX), m.p. 73—74°. (VII) similarly gives (IX) and non-cryst. 2:3:5:1-OMe- $\text{C}_6\text{H}_2\text{Me}_2\text{CH}_2\text{Br}$ . When treated with  $\text{Na}_2\text{CO}_3$ , (IX) passes through the quinonemethide into (II). (VIII) and (VI) are likewise cleaved by HBr. (V) is converted by HBr in cold light petroleum into (IX) in 30% yield. Determinations of mol. wt. (Rast) indicate that (V) at any rate to a considerable extent consists of chain or cyclic mols. composed of 4—5 units of (I) joined to one another by  $\text{Ph-O-CH}_2\text{Ph}$  linkings or alternately with  $\text{CH}_2\text{Ph-O-CH}_2\text{Ph}$  and  $\text{Ph-O-CH}_2\text{Ph}$  linkings. The elimination of  $\text{CH}_2\text{O}$  from (I) is not entirely accounted for by the production of (IV). In presence of xylenol (X), the yield of (III) is < from (I) alone but its formation remains the fastest reaction and added (X) is not involved to > a limited extent. H. W.

Phenol-formaldehyde resins. IX. Mechanism of the hardening of resols: hardening of tri-*p*-cresol dialcohols. S. Kyrning (*Arkiv Kemi, Min., Geol.*, 1941, 15, A, No. 2, 9 pp.; cf. A., 1940, II, 216).—3:5-Di-(2'-hydroxy-5'-methylbenzyl)-*p*-cresol and  $\text{CH}_2\text{O}$ -aq. alkali give 3:5-di-(2'-hydroxy-5'-methyl-3'-hydroxymethylbenzyl)-*p*-cresol (I), m.p. 203° (preheated bath), converted by HBr-EtOH into the corresponding dibromide (II), m.p. 172° (decomp.). Hardening of (I) at 130°, 200°, 220°, or 240° is accompanied by loss of  $\text{H}_2\text{O}$  and  $\text{CH}_2\text{O}$ ; the rate of elimination is examined. Mechanisms of the hardening process involving formation of larger mols. by junction of nuclei through  $-\text{CH}_2\text{O-CH}_2-$  is outlined. (II) is also obtained when the product (insol. in  $\text{CHCl}_3$ ) formed from (I) at 130° is treated with HBr- $\text{CHCl}_3$ . A. T. P.

Phenol-formaldehyde resins. XIII. Mechanism of the hardening of resols. Reaction phases of the hardening of dinuclear dialcohols. H. von Euler, E. Adler, and S. Tingstam (*Arkiv Kemi, Min., Geol.*, 1942, 15, A, No. 10, 11 pp.).—The course of the hardening of 1:5:2:3- (I) and 1:3:4:5- $\text{CH}_2\text{C}_6\text{H}_4\text{Me}(\text{OH})\text{CH}_2\text{OH}$  (II) is best represented as a consequence of ether condensation and quinonemethide formation with subsequent polymerisation and oxido-reduction of the quinonemethide groups. The evolution of  $\text{H}_2\text{O}$  and  $\text{CH}_2\text{O}$  from (I) and (II) is measured at definite intervals at 150°, 170°, 190°, and 210°. Loss of  $\text{CH}_2\text{O}$  is small and >0.2 mol. per mol. of (I) or (II) even at 210°. The amount of  $\text{H}_2\text{O}$  evolved increases rapidly to a max. reached at lower temp. in ~1 hr. and at higher temp. in ~30 min., after which it remains const. The loss of  $\text{H}_2\text{O}$  amounts to 1 mol. per mol. of (I) or (II) at 150° increasing to 1.5—1.6 per mol. at the higher temp. At lower temp. therefore the essential consequence of loss of  $\text{H}_2\text{O}$  is the formation of ether chains; at higher temp. this is accompanied by an almost equally rapid production of quinonemethide. At 150° with max. loss of 1.1 mol. of  $\text{H}_2\text{O}$  per mol. of (I) the resultant resin is completely sol. in  $\text{CHCl}_3$ ; at higher temp. in proportion as this ratio is exceeded the proportion of resin insol. in  $\text{CHCl}_3$  increases. Apparently the "ether-chained" resin is sol. in  $\text{CHCl}_3$  but as methide formation and polymerisation cause mol. enlargement and complexity the solubility diminishes more and more. With (II) a much more rapid diminution of solubility in  $\text{CHCl}_3$  is observed. At 150° (0.5 mol. of  $\text{H}_2\text{O}$  lost) the product is completely sol. whereas at 160° (0.95 mol. lost) 56% of the residue is insol. At higher temp. complete insolubility is rapidly attained. Probably quinonemethide formation occurs sooner with (II) than with (I) and overlaps ether production to a greater extent. (Cf. A., 1943, II, 161.) H. W.

Phenol-formaldehyde resins. XIV. Mechanism of the hardening of resols. Hardening of di- and tetra-alcohols of dihydric phenols. S. Kyrning (*Arkiv Kemi, Min., Geol.*, 1942, 15, B, No. 11, 8 pp.).—Investigation of the loss of  $\text{H}_2\text{O}$  on heating OH- $\text{CH}_2$  derivatives of dihydric phenols confirms the reaction mechanism advanced for the resol hardening of the products from mono- and di-alcohols of monohydric phenols. The loss of  $\text{H}_2\text{O}$  from 1:4:2:5- and 1:2:3:6-(OH) $\text{C}_6\text{H}_3(\text{CH}_2\text{OH})_2$  is in agreement with the simultaneous production of ether, diphenylmethane (I), and quinonemethide (II) derivatives. With 1:4:2:3:5:6-(OH) $\text{C}_6\text{H}_2(\text{CH}_2\text{OH})_2$  formation of (I) is excluded and the quantity of  $\text{H}_2\text{O}$  evolved suggests that ether formation is accompanied by production of (II) as second main action. This assumption is largely confirmed by the behaviour of the corresponding quinone-tetra-alcohol (III) from which the formation of (I) or (II) is impossible: the elimination of  $\text{H}_2\text{O}$  is within the limits required for an exclusive ether condensation. The ready hardening of (III) shows that quinone CO activates  $\text{CH}_2\text{OH}$  in the same manner as does phenolic OH. Etherification of  $\text{CH}_2\text{OH}$  greatly diminishes the reactivity. H. W.

Phenol-formaldehyde resins. XV. Mechanism of the hardening of resols: reaction sequence in the hardening of *o*- and *p*-phenolalcohols. H. von Euler, E. Adler, J. O. Cedwall, and S. Tingstam (*Arkiv Kemi, Min., Geol.*, 1942, 15, A, No. 11, 19

pp.).—Examination of observations made with 2:3:5:1-OH- $\text{C}_6\text{H}_2\text{R}'\text{R}''\text{CH}_2\text{OH}$  ( $\text{R}' = \text{R}'' = \text{Me}$ ;  $\text{R}' = \text{H}$ ;  $\text{R}'' = \text{Me}$ ;  $\text{R}' = \text{Br}$ ,  $\text{R}'' = \text{Me}$ ) and 4:3:5:1-OH- $\text{C}_6\text{H}_2\text{Me}_2\text{CH}_2\text{OH}$  indicates that hardening is due to a concurrence of reactions mainly controlled by the structure of the reacting mols., reaction temp., and duration. Although quant. differentiations cannot yet be made, the *o*-quinonemethides derived from *o*-hydroxybenzyl alcohols and their ethers can react to give dihydroxystilbenes (I) and thence stilbenequinones (II), dihydroxydiphenylethanes (III), dimeric quinonemethides (and thence (III)), and trimeric quinonemethides with succeeding phenolaldehydes and nuclear-methylated phenols, whereas the similarly derived *p*-quinonemethides for structural reasons can give only (I), (II), and (III). Resinols formed at low temp. contain mainly ether bridges with some  $\text{CH}_2$  bridges. To a small extent there is also loss of  $\text{H}_2\text{O}$  with production of quinonemethides and loss of  $\text{CH}_2\text{O}$  leading to diphenylmethanes and possibly "cracking" with production of OH-aldehydes. At higher temp. these reactions occur to an increased extent and are interlocked. In the final stages of the reaction polymerisation of the quinonemethides and stilbenequinones plays a decisive part in the mol. enlargement. The temp. is the decisive factor for the extent to which the ether bridges participate in the secondary reactions. The duration of reaction is of importance only within a certain initial period. Subsequently a condition characteristic for each temp. is reached which then undergoes little further alteration. 4:3:5:1-OH- $\text{C}_6\text{H}_2\text{Me}_2\text{CH}_2\text{OH}$  loses  $\text{H}_2\text{O}$  and  $\text{CH}_2\text{O}$  in a sealed tube at 155° giving di-4-hydroxy-3:5-dimethylbenzyl ether (IV), m.p. 173—175°, converted by boiling AcOH into 4-hydroxy-3:5-dimethylbenzyl acetate (V), m.p. 77°. (IV) is largely unchanged at 175° and at 200° still evolves little  $\text{CH}_2\text{O}$  but gives a small amount of a sublimate of 4:3:5:1-OH- $\text{C}_6\text{H}_2\text{Me}_2\text{CHO}$  (oxime, m.p. 166.5—168°). The residue contains unchanged (IV),  $(\text{CH-C}_6\text{H}_2\text{Me}_2\text{OH})_{1:3:5:6}$ , and  $(\text{CH}_2\text{-C}_6\text{H}_2\text{Me}_2\text{OH})_2$ . (IV) in  $\text{CHCl}_3$  is converted by HBr into 4-hydroxy-3:5-dimethylbenzyl bromide, m.p. 115—116° (decomp.) with AcOH-NaOAc gives (V), which in  $\text{Et}_2\text{O}$  is converted by saturated aq.  $\text{NaHCO}_3$  into 3:5:3':5'-tetramethylstilbene-4:4'-quinone, softens and blackens at 215—217°. This with  $\text{SnCl}_4$  in  $\text{CO}_2$  or  $\text{H}_2$ -PtO<sub>2</sub> in EtOAc gives 4:4'-dihydroxy-3:5:3':5'-tetramethylstilbene, m.p. 237—238° (diacetate, m.p. 236—237°). H. W.

Quinoidation of triaryl compounds. Diphenylbromonaphthylmethyl chlorides. L. C. Anderson and D. Johnston (*J. Amer. Chem. Soc.*, 1943, 65, 239—242).— $\text{MgPhBr}$  and 5:1- $\text{C}_{10}\text{H}_6\text{Br-CO}_2\text{Me}$  (less well, the acid or acid chloride) in boiling PhMe give an impure carbinol (I), converted by  $\text{AcCl}$  into diphenyl-5-bromo-1-naphthylmethyl chloride (II) (62%), m.p. 172—174°, which with  $\text{NPhMe}_3$  in aq.  $\text{CO}_2\text{Me}_2$  gives (I), m.p. 150—151° [with  $\text{HCl-Et}_2\text{O}$  gives only a little (II)]. Attempts to prepare 8:2- $\text{C}_{10}\text{H}_6\text{Br-CO}_2\text{H}$  failed. 5:8:2- $\text{C}_{10}\text{H}_6\text{Br}_2\text{-CO}_2\text{Et}$  gives diphenyl-5:8-dibromo-2-naphthylcarbinol (77%), m.p. 127—128° (the acid chloride gives only an oil), and thence (AcCl) the chloride (III), m.p. 163—164°. 2- $\text{C}_{10}\text{H}_6\text{Br}$ ,  $\text{AcCl}$ , and  $\text{AlCl}_3$  in  $\text{PhNO}_2$  give a 1:1 mixture (1:10 in  $\text{CS}_2$ ) of 6:2- and 2:1- $\text{C}_{10}\text{H}_6\text{Br-COMe}$ , oxidised by  $\text{KOC}$  to acids, which yield Me 6-bromo-2-naphthoate (IV) (42%), m.p. 123—124.5°. The derived acid, m.p. 230° (decomp.) (other methods of prep. give poor yields), and Et ester, m.p. 67—68°, are also described.  $\text{MgPhBr}$  (100% excess) ( $\text{LiPh}$  gives an oil) and (IV) in PhMe give diphenyl-6-bromo-2-naphthylcarbinol, +AcOH, m.p. 99—101°, and thence the chloride (V), m.p. 118—119°. 2:1- $\text{C}_{10}\text{H}_6\text{Br-CO}_2\text{Me}$ , a liquid, gives similarly diphenyl-2-bromo-1-naphthylmethyl chloride (VI), m.p. 203—204°, and thence the carbinol, m.p. 129—131°. 4:1- $\text{C}_{10}\text{H}_6\text{Br-CPh}_2\text{Cl}$  or *p*- $\text{C}_6\text{H}_4\text{Br-CPh}_2\text{Cl-C}_{10}\text{H}_7$ -a with  $\text{AgCl}$  in  $\text{SO}_2$  at room temp. rapidly gives  $\text{AgBr}$  (55—65% in 2.5 days), but none is formed from (II), (III), (V), or (VI) by  $\text{AgCl}$  or  $\text{Ag}_2\text{SO}_4$  in  $\text{SO}_2$ ,  $\text{Me}_2\text{SO}_4$ ,  $\text{PhCN}$ , or  $\text{PhNO}_2$  in 6—30 days, indicating little tendency to form transannular quinonoid compounds. All these halides give red, amorphous products, except (III) which is unchanged in  $\text{SO}_2$ . R. S. C.

Quinoidation of triaryl compounds. Diphenylhydroxynaphthylcarbinols. L. C. Anderson and D. G. Thomas (*J. Amer. Chem. Soc.*, 1943, 65, 234—238).—Unsuccessful attempts are recorded to prepare naphthofuchsones having CO and  $\text{CPh}_2$  in different rings of the  $\text{C}_{10}\text{H}_7$  nucleus. OH- $\text{C}_{10}\text{H}_6\text{-CPh}_2\text{-OH}$  give coloured liquids at or above the m.p. when naphthofuchsones formation is theoretically possible but not when it is impossible. *p*-OH- $\text{C}_6\text{H}_4\text{-CPh}_2\text{-OH}$  in 6%  $\text{H}_2\text{SO}_4$ -AcOH gives the same colour (absorption spectrum) as does *p*-O- $\text{C}_6\text{H}_4\text{-CPh}_2$ .  $\text{C}_{10}\text{H}_7$  derivatives which can give a naphthofuchsones with CO and  $\text{CPh}_2$  in one ring are stabilised in 6%  $\text{H}_2\text{SO}_4$ -AcOH; those which can give no naphthofuchsones rapidly decompose, probably by fluorene formation; stability is intermediate when formation of the naphthofuchsones involves both rings. 1:6:2- $\text{C}_{10}\text{H}_6\text{Br}_2\text{-OH}$  with  $\text{Sn}$ , conc.  $\text{HCl}$ , and EtOH gives 6:2- $\text{C}_{10}\text{H}_6\text{Br-OH}$  and some 6:2- $\text{C}_{10}\text{H}_6\text{Br-OEt}$  (I). 2:1-Oalk- $\text{C}_{10}\text{H}_6\text{-MgBr}$  and  $\text{PhCN}$  in  $\text{C}_6\text{H}_6$ -Et<sub>2</sub>O give 2-ethoxy- (30%), m.p. 88—89°, and 2-methoxy-6-benzoylnaphthalene (45%), m.p. 81—82°, both hydrolysed by aq. HBr-AcOH to 2-hydroxy-6-benzoylnaphthalene (70—80%), m.p. 158—159°. With  $\text{MgPhBr}$  in Et<sub>2</sub>O- $\text{C}_6\text{H}_6$  this gives diphenyl-6-hydroxy-2-naphthylcarbinol (II) (75%), m.p. 170—171° (sealed tube; reddish-purple liquid), also obtained less well from

6 : 2-OH·C<sub>10</sub>H<sub>6</sub>·CO<sub>2</sub>Et by MgPhBr.  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OMe, AcCl, and AlCl<sub>3</sub> in PhNO<sub>2</sub> give 6 : 2-OMe·C<sub>10</sub>H<sub>6</sub>·COMe and thence, successively, (NaOCl) 6 : 2-OMe·C<sub>10</sub>H<sub>6</sub>·CO<sub>2</sub>H, (HBr-AcOH) -OH·C<sub>10</sub>H<sub>6</sub>·CO<sub>2</sub>H, -OH·C<sub>10</sub>H<sub>6</sub>·CO<sub>2</sub>Me, and (MgPhBr) (II). Zn in AcOH reduces (II) to  $\delta$ -benzhydryl-2-naphthol, m.p. (anhyd.) 52° or (+MeOH) 101.5—103°. The Me ester, m.p. 130—131.5°, of 5 : 1-OH·C<sub>10</sub>H<sub>6</sub>·CO<sub>2</sub>H (prep. from 1 : 5-NH<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·SO<sub>3</sub>H modified), Me 8-hydroxy-2-, m.p. 151—152.5°, 7-hydroxy-1-, m.p. 124—126°, and 6-hydroxy-1-naphtholate, m.p. 112—113°, with MgPhBr in Et<sub>2</sub>O·C<sub>6</sub>H<sub>6</sub> give diphenyl-5-hydroxy-1- (63%), m.p. 199—200° (red liquid), -8-hydroxy-2- (67%), m.p. 162—163° (pale liquid), -7-hydroxy-1- (67%), m.p. 231.5—232.5° (pre-heated bath; orange-red liquid), and -6-hydroxy-1-naphthylcarbinol, m.p. 188—190° (pale liquid).  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·OBz and AlCl<sub>3</sub> at 150—165° give 1 : 2-, m.p. 64—65°, but at 100° give 1 : 4-OH·C<sub>10</sub>H<sub>6</sub>·COPh, m.p. 164—165°. R. S. C.

**Fluorine-substituted aromatic acids.** G. P. Hager and E. B. Starkey (*J. Amer. Pharm. Assoc.*, 1943, 32, 44—49).—*o*-, decomp. 106°, *m*-, decomp. 108°, and *p*-C<sub>6</sub>H<sub>4</sub>Me·N<sub>2</sub>BF<sub>4</sub>, decomp. 107°, are converted into *o*-, b.p. 114°/763 mm., *m*-, b.p. 123°/766 mm., and *p*-C<sub>6</sub>H<sub>4</sub>MeF, b.p. 110°/767 mm., respectively, from which are obtained: *o*-, *m*-, and *p*-C<sub>6</sub>H<sub>4</sub>F·CH<sub>2</sub>Br, -C<sub>6</sub>H<sub>4</sub>F·CHO, and *o*-, m.p. 124°, *m*-, m.p. 124.5—125.5°, and *p*-C<sub>6</sub>H<sub>4</sub>F·CO<sub>2</sub>H, m.p. 186°. *o*-, b.p. 110—115°/15 mm., *m*-, b.p. 229°/766 mm., and *p*-C<sub>6</sub>H<sub>4</sub>F·CH<sub>2</sub>CN, b.p. 100—103°/3 mm., and boiling 60% H<sub>2</sub>SO<sub>4</sub>-AcOH give *o*-, m.p. 61—62°, *m*-, (not cryst.), and *p*-C<sub>6</sub>H<sub>4</sub>F·CH<sub>2</sub>·CO<sub>2</sub>H, m.p. 82°, respectively. *o*-, m.p. 180—181°, *m*-, m.p. 166.5°, and *p*-fluorocinnamic acid, m.p. 209.5°, and *o*-, m.p. 116.5°, *m*-, m.p. 101°, and *p*-fluoromandelic acid, m.p. 133°, are prepared from C<sub>6</sub>H<sub>4</sub>F·CHO. The antibacterial activity of the above F-acids is determined. Although introduction of *p*-Cl, -Br, or -I doubles the toxicity (white rats) of BzOH, *p*-F has little effect. A. T. P.

**Optically active nitro- and amino-mandelic acids.** II. A. Fredga and E. Andersson (*Arkiv Kemi, Min., Geol.*, 1941, 14, B, No. 38, 7 pp.).—*p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHBr·COCl with warm aq. NaHCO<sub>3</sub> gives *r*-*p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH(OH)·CO<sub>2</sub>H (I), m.p. 126—127°, in 65% yield. It is resolved by quinidine in boiling aq. EtOH into (+)-*p*-nitromandelic acid, (II) m.p. 93—94°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +128.9°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +151.8° in H<sub>2</sub>O [quinidine and Pb (+1H<sub>2</sub>O) salts]. The acid remaining in the mother-liquors after removal of (II) is resolved by strychnine in boiling 30% EtOH into (–)-*p*-nitromandelic acid (III), m.p. 93—94°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> –129.2°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> –152.1° in H<sub>2</sub>O [strychnine (+2H<sub>2</sub>O) salt]. (I) as Na salt in H<sub>2</sub>O is reduced (H<sub>2</sub>-Pd-C) to *r*-*p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH(OH)·CO<sub>2</sub>H (IV), decomp. 205—210° after becoming discoloured. Similarly (II) gives (+)- (V), decomp. >200°, becomes yellow at ~140° and brown at 200°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +106.9°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +128.7° in 0.1N-NaOH, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +133.0°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +157.3° in N-HCl, and (III) gives (–)-*p*-aminomandelic acid (VI), [ $\alpha$ ]<sub>D</sub><sup>25</sup> –106.5° in 0.1N-NaOH. (IV) is transformed through the diazo-compound into *r*-OH·CHPh·CO<sub>2</sub>H, and (V) into (+)-OH·CHPh·CO<sub>2</sub>H, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +153° in H<sub>2</sub>O. (II) and (V) have therefore the same configuration as *l*-(+)-mandelic acid whereas (III) and (VI) are related to the *d*-(–)-acid. H. W.

**Lactones related to the cardiac aglycones.** XI. Synthesis of  $\beta$ -substituted  $\Delta^{\alpha\beta}$ -butenolides from methyl ketones. E. R. Blout and R. C. Elderfield (*J. Org. Chem.*, 1943, 8, 29—36).—The possibility of preparing these compounds by methods involving the removal of a substituent in the  $\alpha$ -position of the requisite butyrolactones has been explored. Addition of cyclohexyl Me ketone (I) and CHCl<sub>2</sub>·CO<sub>2</sub>Et in Et<sub>2</sub>O to Mg-Hg gives Et  $\alpha$ -chloro- $\beta$ -hydroxy- $\beta$ -cyclohexylbutyrate, b.p. 110—135°/1.8 mm., converted by HBr in boiling glacial AcOH into  $\alpha$ -chloro- $\beta$ -cyclohexylbutyrolactone (II), b.p. 131—135°/0.9 mm., m.p. 131—131.5°. (II) is largely resinified by boiling quinoline whilst boiling NPhMe<sub>2</sub> causes only partial removal of HCl with formation of obscure condensation products; C<sub>6</sub>H<sub>5</sub>N is without action. Boiling 4% aq. NaOH partly converts (II) into  $\alpha$ -hydroxy- $\beta$ -cyclohexylbutyrolactone, m.p. 144° (*p*-nitrobenzoate, m.p. 154—154.5°), whilst anhyd. KOAc in boiling AcOH gives  $\beta$ -cyclohexyl- $\Delta^{\alpha\beta}$ -butenolide [ $\beta$ -cyclohexyl- $\Delta^{\alpha}$ -butenolactone] (III), b.p. 115—117°/0.1 mm., further identified by conversion into Me  $\beta$ -formyl- $\beta$ -cyclohexylpropionate (semicarbazone, m.p. 118—119°). Addition of (I) and CH<sub>2</sub>Cl·CO<sub>2</sub>Et to NaOEt-EtOH at –80° gives Et  $\alpha\beta$ -oxido- $\beta$ -cyclohexylbutyrate, b.p. 86—90°/0.3 mm., converted by boiling HBr-AcOH into a material with an odour of (III) but contaminated with other substances of approx. the same b.p. CPhMe, CHCl<sub>2</sub>·CO<sub>2</sub>Et, and Mg-Hg afford OH·CPhMe·CHCl·CO<sub>2</sub>Et (IV), b.p. 124—126°/1.5 mm., with some (CPhMe·OH)<sub>2</sub>. (IV) and boiling HBr-AcOH yield CPhMe, Et  $\alpha$ -chloro- $\beta$ -phenylcrotonate, b.p. 103°/5 mm., and  $\beta$ -phenyl- $\Delta^{\alpha\beta}$ -butenolide, m.p. 93°. Et  $\beta$ -hydroxy- $\beta$ -cyclohexylbutyrate is converted by boiling HBr-AcOH into  $\beta$ -cyclohexylbutyrolactone, b.p. 124—126°/1.2 mm. (yield 79%), also obtained in 78% yield by use of boiling H<sub>2</sub>SO<sub>4</sub>-AcOH-H<sub>2</sub>O. It is brominated in boiling glacial AcOH to  $\beta$ -x-bromocyclohexylbutyrolactone (V), b.p. 130—135°/1 mm., m.p. 63—63.5°, converted by 2N-NaOH and subsequent acidification into  $\beta$ -x-hydroxycyclohexylbutyrolactone (VI), b.p. 140—152°/0.7 mm. (*p*-nitrobenzoate, m.p. 163—164.5°). (VI) is oxidised by CrO<sub>3</sub> in 90% AcOH at  $\leq$ 30° to  $\beta$ -x-ketocyclohexylbutyrolactone, m.p. 82—83.5° [*p*-nitrophenylhydraz-

one, m.p. 187—188° (decomp.) (softens at 184°); *N*-OH-derivative, m.p. 160—161° (decomp.)]. Anhyd. KOAc, boiling AcOH, and (V) appear to give a mixture of acetoxycyclohexyl- and cyclohexenylbutyrolactone, b.p. 110—114°/0.2 mm. M.p. and b.p. are corr. H. W.

**Lactones related to the cardiac aglycones.** XII. Condensation of ethyl oxalate with ethyl  $\gamma$ -cyclohexylcrotonate and a method for predicting the products from such condensations. E. R. Blout, J. Fried, and R. C. Elderfield (*J. Org. Chem.*, 1943, 8, 37—42).—Past (A., 1942, II, 28, 29) and present experiences of the authors with those of Kuhn *et al.* (A., 1937, II, 438) and Boese *et al.* (A., 1934, 632) show that in condensations involving Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and  $\gamma$ -substituted  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -crotonic esters and their vinyllogues, the position originally occupied by the double linking is of little importance and the controlling factor is the electronic nature of the substituent at C<sub>(\gamma)</sub>. Condensation occurs in the  $\gamma$ -position if this is H. If the  $\gamma$ -substituent is a *n*-alkyl, condensation takes place at C<sub>(\gamma)</sub> with progressively poorer yields as the inductive effect of the substituent increases. When the electron-donating capacity of the  $\gamma$ -substituent is still further enhanced, as in the case of the cyclohexyl group, condensation occurs at C<sub>(\alpha)</sub>; aryl substituents lead to condensation in this position. C<sub>6</sub>H<sub>5</sub>N, used as solvent, has no effect on the course of the condensation. Gradual addition of Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in dry Et<sub>2</sub>O to KOEt in EtOH-Et<sub>2</sub>O at 0° and subsequent addition of Et  $\gamma$ -cyclohexylcrotonate in dry C<sub>6</sub>H<sub>5</sub>N to the mixture at 0° gives Et  $\gamma$ -keto- $\beta$ -carbethoxy- $\delta$ -cyclohexyl- $\Delta^{\gamma}$ -pentenoate (I) as a heavy yellow oil which could not be cryst. or distilled without decomp. (2 : 4-dinitrophenylhydrazones, m.p. 76—77°). It is hydrolysed by conc. HCl-AcOH at room temp. to  $\alpha$ -keto- $\beta$ -carbethoxy- $\delta$ -cyclohexyl- $\Delta^{\gamma}$ -pentenoic acid, m.p. 83.5—84° (*p*-bromophenacyl ester, m.p. 108—109°), and the corresponding  $\beta$ -carboxy-acid, m.p. 217° after decomp. from 135°. Boiling conc. HCl-AcOH converts either ester into  $\alpha$ -keto- $\delta$ -cyclohexyl- $\Delta^{\gamma}$ -pentenoic acid, m.p. 93—94°, which gives a red colour with FeCl<sub>3</sub> in EtOH, and is transformed by boiling Ac<sub>2</sub>O into the corresponding lactone acetate, C<sub>6</sub>H<sub>11</sub>·CH<CH<sub>2</sub>·CH<O>CO>C·OAc, m.p. 87—88°. (I) is reduced (H<sub>2</sub>-PtO<sub>2</sub> in abs. EtOH) and then hydrolysed (KOH) to  $\alpha$ -hydroxy- $\beta$ -carboxy- $\delta$ -cyclohexyl-*n*-valeric acid (III), m.p. 126—127° (*di*-*p*-bromophenacyl ester, m.p. 143—144°). Et  $\gamma$ -cyclohexylbutyrate, b.p. 86—87°/0.6 mm., is condensed with Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> to Et  $\alpha$ -keto- $\beta$ -carbethoxy- $\delta$ -cyclohexyl-*n*-valerate (2 : 4-dinitrophenylhydrazones, m.p. 81—82.5°), reduced and hydrolysed to (II). H. W.

**Addition of sodium triphenylmethyl and lithium phenyl to cinnamic ester and benzylideneacetophenone.** A. Michael and C. M. Saffer, jun. (*J. Org. Chem.*, 1943, 8, 60—63).—Me  $\beta\gamma\gamma\gamma$ -tetraphenylbutyrate (I), m.p. 170.5—171° (acid, m.p. 227—228°), is obtained in modest yield by addition of CPh<sub>3</sub>Na in anhyd. Et<sub>2</sub>O to CHPh·CH·CO<sub>2</sub>Me (II) in Et<sub>2</sub>O and N<sub>2</sub> at –20°. Considerable polymerisation and formation of tar seem to occur and reactions of this type are only successful in the complete absence of moisture and enolisable H. Et  $\beta\gamma\gamma\gamma$ -tetraphenylbutyrate, m.p. 127—127.5°, is obtained similarly from CHPh·CH·CO<sub>2</sub>Et. Pyrolysis of (I) gives CHPh<sub>3</sub> and CHPh·CH·CO<sub>2</sub>H. CHMe·CH·CO<sub>2</sub>Et does not appear to give an additive compound with CPh<sub>3</sub>Na.  $\alpha\alpha\beta\gamma\gamma$ -Pentaphenylpropanol (III), m.p. 160.5—161°, obtained by addition of LiPh in Et<sub>2</sub>O to (II) in Et<sub>2</sub>O and N<sub>2</sub> at –20°, passes at 180—200°/4 mm. into  $\alpha\alpha\beta\gamma\gamma$ -pentaphenylpropene, m.p. 214—215°. Li cinnamate has m.p. 303—305° (decomp.). With CPh<sub>3</sub>·CH·CHPh, LiPh affords CHPh·CH·CPh<sub>2</sub>·OH, m.p. 110—111°, and (III). M.p. are corr. H. W.

**3 : 4-Dinitrobenzoic acid.** H. Goldstein and R. Voegeli (*Helv. Chim. Acta*, 1943, 26, 475—481).—In compounds 3 : 4 : 1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>X when X is a substituent of the first order (Cl, Br, Me, OMe) the NO<sub>2</sub> at C<sub>(3)</sub> is mobile but when X is a substituent of the second order (NO<sub>2</sub>, CO<sub>2</sub>H) the mobility is shown by NO<sub>2</sub> at C<sub>(4)</sub>. 3 : 4 : 1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>H (I) [prep. from 1 : 3 : 4-C<sub>6</sub>H<sub>3</sub>Me(NO<sub>2</sub>)<sub>2</sub> described] is converted into the chloride, b.p. 204—205°/17 mm., 188°/11 mm., m.p. 50—51°, Me ester, m.p. 87°, amide, m.p. 165—166°, and anilide, m.p. 188—189°. With the appropriate reagent it affords 3-nitro-4-hydroxy-, -4-methoxy-, -4-amino-, -4-dimethylamino-, and -4-anilino-benzoic acid. (I) and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in boiling EtOH afford 4 : 3 : 1-NH<sub>2</sub>·NH·C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)·CO<sub>2</sub>H, which could not be purified by itself or as N<sub>2</sub>H<sub>4</sub> salt (II) but is characterised by its Ac, m.p. 276—278° (decomp.), and CMe<sub>2</sub>, m.p. 243°, derivatives. (II) is transformed by 10% Na<sub>2</sub>CO<sub>3</sub> at 100° into 1-hydroxy-1 : 2 : 3-benzotriazole-6-carboxylic acid, decomp. without melting at ~225°, deflagrates at 245—247°. 3-Nitro-4-phenylhydrazinobenzoic acid, m.p. 241°, changes at ~205°, is transformed by boiling glacial AcOH into 6-carboxy-2-phenyl-2 : 1 : 3-benzotriazole 1-oxide, m.p. 250°. M.p. are corr. H. W.

**2-Bromo-4 : 5-dinitrobenzoic acid.** H. Goldstein and G. Gianola (*Helv. Chim. Acta*, 1943, 26, 173—181).—4 : 2 : 1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Br·CO<sub>2</sub>H (prep. from *o*-toluidine described) is converted by HNO<sub>3</sub> (*d* 1.54) and conc. H<sub>2</sub>SO<sub>4</sub> at room temp. and finally at 100° into 2-bromo-4 : 5-dinitrobenzoic acid (I), m.p. 184°. Its constitution is established by its conversion by conc. aq. NH<sub>3</sub> at room temp. into 2-bromo-5-nitro-4-aminobenzoic acid, m.p. 264° (Ac derivative, m.p. 205°), deaminated to 5 : 2 : 1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Br·CO<sub>2</sub>H (II) anhyd. K CO<sub>3</sub>

and  $\text{NH}_2\text{Ph}$  at  $100^\circ$  yield 2-bromo-5-nitro-4-anilinobenzoic acid, m.p.  $253.5^\circ$ , transformed by boiling  $\text{NH}_2\text{Ph}$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{Cu}$  powder into  $5:2:4:1\text{-NO}_2\cdot\text{C}_6\text{H}_2(\text{NHPh})_2\cdot\text{CO}_2\text{H}$  and  $[\text{C}_6\text{H}_2(\text{NO}_2)(\text{NHPh})\cdot\text{CO}_2\text{H}]_4$ . (I) and boiling  $2\text{N-NaOH}$  or  $\text{MeOH-KOH}$  at  $50^\circ$  yield 2-bromo-5-nitro-4-hydroxy-, m.p.  $221^\circ$ , or 4-methoxy-benzoic acid, m.p.  $250^\circ$ , respectively. 2-Bromo-5-nitro-4-dimethylaminobenzoic acid, m.p.  $232^\circ$  (decomp.), is obtained from (I) and aq.  $\text{NHMe}_2$  at  $100^\circ$ .  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  and (I) readily yield 2-bromo-5-nitro-4-hydrazinobenzoic acid, m.p.  $167^\circ$  (decomp.) [ $\text{Ac}$ , m.p.  $263.5^\circ$ , and  $\text{CMe}_2$ , m.p.  $244^\circ$  (decomp.)], derivatives, transformed by boiling  $2\text{N-Na}_2\text{CO}_3$  into 6-bromo-3-hydroxybenzotriazole-5-carboxylic acid, deflagrates without melting at  $211^\circ$ . 2-Bromo-5-nitro-4-phenylhydrazinobenzoic acid, m.p.  $\sim 180^\circ$  when heated very rapidly or  $231^\circ$  (becomes yellow-brown at  $170\text{--}175^\circ$ ) when heated slowly, is converted by boiling  $\text{AcOH}$  into 6-bromo-3-oxido-2-phenylbenzotriazole-5-carboxylic acid, orange or yellow needles, m.p.  $236^\circ$ . (I) is reduced by  $\text{SnCl}_2$  and conc.  $\text{HCl}$  to 2-bromo-4:5-diaminobenzoic acid dihydrochloride (II); the free acid blackens almost immediately on contact with air and is characterised as its  $\text{Ac}_2$  derivative, m.p.  $257^\circ$ . (II) is transformed by more prolonged treatment with  $\text{NaOAc}$  and boiling  $\text{Ac}_2\text{O}$  into 6-bromo-2-methylbenzimidazole-5-carboxylic acid, m.p.  $323^\circ$ , and by  $\text{HNO}_3$  into 6-bromobenzotriazole-5-carboxylic acid, m.p.  $\sim 325^\circ$  (decomp.). (II) is converted by  $\text{Ac}_2$  in boiling  $\text{H}_2\text{O}$  into 7-bromo-2:3-dimethyl-, m.p.  $278^\circ$  (decomp.), and by  $\text{NaOAc}$  and  $\text{Bz}_2$  in boiling abs.  $\text{EtOH}$  into 7-bromo-2:3-diphenyl-, m.p.  $234.5^\circ$ , -quinoline-6-carboxylic acid. M.p. are corr. H. W.

**Nitration of  $\beta$ -polyalkylphenylisovaleric acids. II.  $\beta$ -m-5-Xylyl-isovaleric acid.** L. I. Smith and L. J. Spillane (*J. Amer. Chem. Soc.*, 1943, **65**, 282—289).—The structure of  $2:6:3:4:5:1\text{-(NO}_2)_2\text{C}_6\text{Me}_3\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$  (A., 1940, II, 230) is confirmed by the behaviour of related compounds. Adding  $\text{KNO}_3\text{--H}_2\text{SO}_4$  to  $3:5:1\text{-C}_6\text{H}_3\text{Me}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$  (I) in  $\text{CHCl}_3\text{--H}_2\text{SO}_4$  at  $-15^\circ$  to  $5^\circ$  gives a small amount of  $\text{Me } \beta\text{-2:4-dinitro-m-5-xylylisovalerate}$  (II), m.p.  $73.5\text{--}74^\circ$ , and a larger amount of an oily nitrosulphonic acid.  $65\%$  of (II) is obtained in  $\text{CHCl}_3$  alone at  $<5\text{--}10^\circ$ . Boiling  $\text{Ac}_2\text{O--H}_2\text{SO}_4$  or  $\text{HCl}$  at  $100^\circ$  does not affect (II).  $\text{H}_2\text{--PtO}_2$  reduces (II) in  $\text{MeOH}$  at 38 lb. to an amine, m.p.  $86.5\text{--}90^\circ$  ( $\text{Ac}$  derivative, m.p.  $138.5\text{--}139.5^\circ$ ), of unknown structure. Dil.  $\text{HNO}_3\text{--H}_2\text{O}_2\text{--AcOH}$ ,  $\text{KMnO}_4\text{--AcOH}$ , or  $\text{NaOH--MeOH}$  with (I) yields indefinite products.  $\text{H}_2\text{SO}_4$  at room temp. hydrolyses (II) to the acid, m.p.  $153\text{--}154.5^\circ$  [with  $\text{H}_2\text{SO}_4\text{--MeOH}$  regenerates (II)], which with  $\text{Cu}$  chromite in quinoline at  $225\text{--}235^\circ$  yields an oil and gives indefinite products (no  $\text{HNO}_2$ ) with  $\text{NaOMe--MeOH}$ . With  $\text{HNO}_3$  ( $d$  1.5) and  $\text{H}_2\text{SO}_4$  at  $3^\circ$  room temp., (I) or (II) gives  $\text{Me } \beta\text{-2:4:6-trinitro-m-5-xylylisovalerate}$  (III), m.p.  $127\text{--}127.5^\circ$ , converted by  $\text{NaOH--aq. MeOH}$  into a substance, m.p.  $234\text{--}244^\circ$  (decomp.), and by conc.  $\text{H}_2\text{SO}_4$  into the acid, m.p.  $194\text{--}198.5^\circ$  (decomp.). With  $\text{Cu}$  chromite in quinoline- $\text{N}_2$  at  $170\text{--}175^\circ$ , this acid gives  $5:7\text{-dinitro-4:4:6:8-tetramethyl-3:4-dihydrocoumarin}$  (IV), m.p.  $163.5\text{--}164^\circ$ , slowly sol. in  $4\text{N-NaOH}$ , reduced by  $\text{Zn--80\% AcOH}$  to a phenol and by  $\text{H}_2\text{S--NH}_3\text{--aq. EtOH}$  at  $100^\circ$  to impure 5-nitro-7-amino-4:4:6:8-tetramethyl-3:4-dihydrocoumarin, softens  $188^\circ$ , m.p.  $192\text{--}197^\circ$ .  $m\text{-4-xylenol}$ ,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$  (V),  $\text{AlCl}_3$ , and  $\text{HCl}$  in light petroleum at  $<0^\circ$  (later the b.p.) give  $4:4:6:8\text{-tetramethyl-3:4-dihydrocoumarin}$  (45%), m.p.  $104.5\text{--}105^\circ$ , which with  $\text{HNO}_3$  ( $d$  1.5) in  $\text{H}_2\text{SO}_4$  gives (IV) (proof of structure).  $\text{H}_2\text{S--NH}_3\text{--aq. MeOH}$  at  $100^\circ$  reduces (II) to  $\text{Me } \beta\text{-4-nitro-2-amino-m-5-xylylisovalerate}$ , m.p.  $91\text{--}92^\circ$  ( $\text{Ac}$  derivative, m.p.  $138.5\text{--}139^\circ$ ), hydrolysed by boiling  $6\text{N-HCl}$  to the acid, m.p.  $176.5\text{--}179^\circ$  (decomp.) ( $\text{Ac}$  derivative, m.p.  $187.5\text{--}180^\circ$ , resists ring-closure).  $2:6:1\text{-C}_6\text{H}_3\text{Me}_2\cdot\text{NHAc}$  (VI), m.p.  $179\text{--}180^\circ$  (lit.  $177^\circ$ ), (V),  $\text{HCl}$ , and  $\text{AlCl}_3$  in  $\text{C}_2\text{H}_2\text{Cl}_4$  at  $5^\circ$  give only an oil.  $\text{Bu}^\beta\text{CO}_2\text{H}$  with  $\text{SO}_2\text{Cl}_2\text{--Bz}_2\text{O}_2$  in boiling  $\text{CCl}_4$  and then  $\text{H}_2\text{SO}_4\text{--MeOH}$  gives  $\text{Me } \beta\text{-chloroisovalerate}$  (28%), b.p.  $69\text{--}72^\circ/17\text{ mm.}$ , which with  $\text{NaOH}$  gives (V) but cannot be condensed with (VI).  $\text{HNO}_3$  ( $d$  1.5) in  $\text{AcOH--Ac}_2\text{O}$  at  $<20^\circ$  (later  $50^\circ$ ) converts (I) into  $\text{Me } 4\text{-nitro-m-5-xylylisovalerate}$  (VII) (87%), b.p.  $153\text{--}155^\circ/5\text{ mm.}$ , hydrolysed by alkali to the acid (VIII), m.p.  $134\text{--}136^\circ$ , which is also obtained (m.p.  $135\text{--}136^\circ$ ) by similarly nitrating the corresponding acid. The structure of (VII) is proved by reduction by  $\text{Zn--80\% AcOH}$  to  $4:4:6:8\text{-tetramethylhydrocarboxystyryl}$ , m.p.  $150\text{--}151^\circ$  [also obtained from (VIII)].  $\text{HNO}_3$  ( $d$  1.5) in  $\text{H}_2\text{SO}_4$  at  $0^\circ$  converts (VII) into (III); under other conditions some (II) can be isolated from mixed products. R. S. C.

**Polyalkylbenzenes. XXXII. Reaction between dimethylacrylic acid and  $m$ -xylene.** L. I. Smith and L. J. Spillane (*J. Amer. Chem. Soc.*, 1943, **65**, 202—208; cf. A., 1941, II, 6).— $m$ -Xylene,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , and  $\text{AlCl}_3$  at  $-8^\circ$  to room temp. give  $\beta\text{-m-5-xylylisovaleric acid}$  (I) (97%), m.p.  $111\text{--}112^\circ$  [ $\text{Me}$  ester (II), b.p.  $134\text{--}137^\circ/11\text{ mm.}$ ], cyclised in  $\text{H}_2\text{SO}_4$  at room temp. to  $3:3:5:7\text{-tetramethylhydrindone}$  (III), m.p.  $57.5\text{--}58^\circ$  (oxime, m.p.  $154.5\text{--}155^\circ$ ), which is probably the same as the hydrindone, m.p.  $62\text{--}63^\circ$ , of Smith *et al.* (A., 1940, II, 224).  $m$ -Xylene,  $\text{CMe}_2\cdot\text{CH}\cdot\text{COCl}$ , and  $\text{AlCl}_3$  in  $\text{CS}_2$  at  $0\text{--}35^\circ$  give  $4\text{-}\beta\text{-methylcrotonyl-}m\text{-xylene}$  (61%), b.p.  $137\text{--}139^\circ/15\text{ mm.}$ , converted by  $\text{O}_3$  in  $\text{AcOH}$  or  $\text{KMnO}_4$  in  $\text{COMe}_2$  into  $2:4:1\text{-C}_6\text{H}_3\text{Me}_2\cdot\text{CO}_2\text{H}$  and by treating with  $\text{HCl--AlCl}_3$  (excess) in  $\text{CS}_2$  and evaporating (not other conditions) into (III) (48%) and tar. This proves the structure of (III) and probably also of (I).  $2:4:1\text{-C}_6\text{H}_3\text{Me}_2\cdot\text{COMe}$  and  $\text{MgMeBr}$  in boiling  $\text{Et}_2\text{O}$  give  $\beta\text{-m-4-}$

$\text{xylylpropan-}\beta\text{-ol}$  (IV) (88%), b.p.  $88\text{--}90^\circ/2\text{ mm.}$ , the bromide (prep. by  $\text{PBr}_3\text{--Et}_2\text{O}$ ) from which with  $\text{CHNa}(\text{CO}_2\text{Et})_2\text{--EtOH}$  gives (?)  $2:4:1\text{-C}_6\text{H}_3\text{Me}_2\cdot\text{CMe}\cdot\text{CH}_2$ , b.p.  $82\text{--}82.5^\circ/18\text{ mm.}$ ; the corresponding chloride (prep. by  $\text{HCl}$  in light petroleum at  $0^\circ$ ) with anhyd.  $\text{K}_2\text{CO}_3\text{--MeOH}$  at room temp. gives the  $\text{Me}$  ether, b.p.  $62.5\text{--}65^\circ/2\text{ mm.}$ , of (IV), which with  $\text{K}$  etc. and then  $\text{CO}_2$  gives only oils. Only oils are obtained from  $1:3:5\text{-C}_6\text{H}_3\text{Me}_2\text{Pr}^\beta$  by  $\text{KCH}_2\text{Ph}$  and then  $\text{CO}_2$ .  $3:5:1\text{-C}_6\text{H}_3\text{Me}_2\cdot\text{CH}_2\cdot\text{CN}$  with  $\text{NaNH}_2$  and then  $\text{MeI}$  in  $\text{Et}_2\text{O}$  gives  $\alpha\text{-m-5-xylylisobutyronitrile}$  (impure), b.p.  $131^\circ/25\text{ mm.}$  (in liquid  $\text{NH}_3$  much  $s\text{-C}_6\text{H}_3\text{Me}_3$  is formed), which in  $85\%$   $\text{H}_2\text{SO}_4$  at  $100^\circ$  gives the amide (33%), m.p.  $109.5\text{--}110.5^\circ$ . Boiling  $25\%$   $\text{H}_2\text{SO}_4$  then gives the acid (V), m.p.  $116.5\text{--}117.5^\circ$ , the chloride (prep. by  $\text{SOCl}_2$  and  $\text{C}_6\text{H}_5\text{N}$ ) of which with  $\text{CH}_2\text{N}_2\text{--C}_6\text{H}_5\text{--Et}_2\text{O}$  at  $0^\circ$ ,  $\text{Ag}_2\text{O--MeOH}$ , and then  $\text{NaOH--aq. MeOH}$  gives only traces of acid.  $\text{MgMeI}$  and (II) in  $\text{Et}_2\text{O}$  give a product, converted by boiling  $\text{AcOH}$  + a trace of  $\text{H}_2\text{SO}_4$  into  $1:1:3:3:4:6\text{-hexamethylindane}$ , b.p.  $114\text{--}117^\circ/13\text{ mm.}$ , indifferent to  $\text{KMnO}_4$  and  $\text{O}_3\text{--EtBr}$ . Decarboxylation of (I) gives a mixture. Boiling  $\text{KMnO}_4\text{--NaOH--H}_2\text{O}$  oxidises (V) and (I) to  $\alpha\text{-3:5-dicarboxyphenylisobutyric}$  (VI), m.p.  $298\text{--}300^\circ$  ( $\text{Me}_3$  ester, m.p.  $73.5\text{--}76.5^\circ$ ), and -valeric acid, m.p.  $247\text{--}250^\circ$  (also formed with  $\text{HNO}_3\text{--H}_2\text{O}$  at  $198\text{--}200^\circ$ ;  $\text{Me}_3$  ester, m.p.  $68.5\text{--}69.5^\circ$ ), respectively. R. S. C.

**Rearrangement of phenyl allyl ethers. VII. Isomeric ethyl  $p$ - $\alpha$ - and  $\gamma$ -methylallyloxybenzoates.** W. M. Lauer and P. A. Sanders (*J. Amer. Chem. Soc.*, 1943, **65**, 198—201; cf. A., 1940, II, 15).— $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$  (I) and  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$  in boiling  $\text{NaOEt--EtOH}$  give  $\text{Et } p\text{-}\Delta\beta\text{-butenoxybenzoate}$  (II), m.p.  $51\text{--}51.5^\circ$ , and thence ( $\text{KOH--MeOH}$ ) the derived acid, m.p.  $176.5\text{--}178^\circ$ , hydrogenated to  $p\text{-OBu}^\alpha\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , also obtained from (I) by  $\text{Bu}^\alpha\text{Br--NaOEt--EtOH}$ . Ozonolysis of (II) gives  $\text{MeCHO}$  (proof of structure). At  $210\text{--}227^\circ$ , (II) gives  $\text{Et } 4\text{-hydroxy-3-}\alpha\text{-methylallylbenzoate}$  (III), m.p.  $76\text{--}78^\circ$ , converted by boiling  $\text{NaOMe--MeOH--Me}_2\text{SO}_4$  and then hot  $20\%$  aq.  $\text{NaOH}$  into  $4\text{-methoxy-3-}\alpha\text{-methylallylbenzoic acid}$ , m.p.  $159\text{--}160^\circ$ , which with  $\text{O}_3$  in  $\text{EtBr}$  gives  $\text{CH}_2\text{O}$  (proof of structure). With  $\text{KOH--MeOH}$ , (III) gives the derived acid, m.p.  $113\text{--}114^\circ$ , which by heating in quinoline and then treating with  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et--NaOH}$  yields, after hydrolysis,  $o\text{-CH}_2\cdot\text{CH}\cdot\text{CHMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m.p.  $125^\circ$  (lit.  $120\text{--}120.5^\circ$ ).  $\text{CH}_2\cdot\text{CH}\cdot\text{CHMeCl}$  and (I) give similarly  $\text{Et } p\text{-}\alpha\text{-methylallyloxybenzoate}$  (IV) and (III), separated by way of the acids;  $p\text{-}\alpha\text{-methylallyloxybenzoic acid}$ , m.p.  $155\text{--}156^\circ$ , gives (IV) by way of the  $\text{Ag}$  salt and with  $\text{H}_2\text{--Pd--CaCO}_3$  yields  $p\text{-sec-butoxybenzoic acid}$ , m.p.  $119\text{--}120^\circ$ , also obtained from (I) by  $\text{CHMeEtBr--NaOEt--EtOH}$  etc. With  $\text{O}_3$  in  $\text{EtBr}$ , (IV) gives  $\text{CH}_2\text{O}$ . At  $222\text{--}240^\circ$  (IV) gives  $3:4:1\text{-CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{Et}$  (V), m.p. (crude)  $69\text{--}75^\circ$ , and a little  $(\text{CH}_2\cdot\text{CH})_2$ . Hydrolysis of (V) gives  $4\text{-hydroxy-3-}\Delta\beta\text{-butenylbenzoic acid}$  (VI), m.p.  $115\text{--}116^\circ$ .  $\text{Me}_2\text{SO}_4\text{--NaOMe--MeOH}$  and then hot  $25\%$   $\text{KOH--MeOH}$  convert (V) into  $4\text{-methoxy-3-}\Delta\beta\text{-butenylbenzoic acid}$  (VII), m.p.  $150\text{--}151.5^\circ$ , and (?) an impure isomeride. Ozonolysis of (VII) gives  $\text{MeCHO}$  and a little  $\text{CH}_2\text{O}$ ; hydrogenation gives  $4\text{-methoxy-3-n-butylbenzoic acid}$ , m.p.  $131.5\text{--}132.5^\circ$ .  $\text{Me } 2\text{-methoxy-5-carbomethoxyphenylacetate}$ , m.p.  $79\text{--}80^\circ$ , is obtained from (VII) or  $3:4:1\text{-CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CO}_2\text{H}$  by  $\text{KMnO}_4\text{--COMe}_2$  at room temp. and esterification of the products by way of the  $\text{Ag}$  salts. (See A., 1943, II, 205.) R. S. C.

**[Attempted] synthesis of aldehydes from acyl hydrazides.** C. Niemann and J. T. Hays (*J. Amer. Chem. Soc.*, 1943, **65**, 482—484).—*Benzenesulphon-o-nitrobenzhydrazide* (prep. from  $\text{PhSO}_2\text{Cl}$  and  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$  in  $\text{C}_6\text{H}_5\text{N}$  at  $10^\circ$ ), m.p.  $184\text{--}184.5^\circ$ , with  $\text{Na}_2\text{CO}_3$  in  $(\text{CH}_2\cdot\text{OH})_2$  at  $160^\circ$  gives no  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ . *Benzenesulphon-p-nitrobenzhydrazide*, m.p.  $201\text{--}202^\circ$ , under these conditions gives  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  and  $\text{PhSO}_2\text{Na}$ . R. S. C.

**Production of amidines.**—See B., 1943, II, 172.

**Addition of dienes to di- $o$ -methoxycinnamic acids. II.** R. Adams and R. B. Carlin (*J. Amer. Chem. Soc.*, 1943, **65**, 360—363).— $1:3:5\text{-C}_6\text{H}_3\text{Me}(\text{OMe})_2$  with  $\text{Li--Bu}^\alpha\text{Cl}$  and then  $\text{NPhMe}\cdot\text{CHO--Et}_2\text{O}$  at room temp. and later the b.p. gives  $3:5:1:4\text{-(OMe)}_2\text{C}_6\text{H}_2\text{Me}\cdot\text{CHO}$ , m.p.  $91\text{--}92^\circ$  (lit.  $90\text{--}91^\circ$ ), which with  $\text{CH}_2(\text{CO}_2\text{H})_2\text{--C}_6\text{H}_5\text{N}$ -piperidine at  $100^\circ$  gives  $2:6\text{-dimethoxy-4-methylcinnamic acid}$  (98%), m.p.  $202^\circ$  (decomp.), converted by  $(\text{CH}_2\cdot\text{CMe})_2$  in xylene at  $170^\circ$  into  $2':6'\text{-dimethoxy-4:5:4'-trimethyl-1:2:3:6-tetrahydrodiphenyl-2-carboxylic acid}$ , m.p.  $178\text{--}180^\circ$ .  $1:3:5\text{-n-C}_6\text{H}_{11}\cdot\text{C}_6\text{H}_3(\text{OMe})_2$  gives similarly  $2:6\text{-dimethoxy-4-n-amyl-benzaldehyde}$ , b.p.  $148\text{--}152^\circ/0.3\text{ mm.}$ , and -cinnamic acid, m.p.  $179^\circ$  (decomp.), which with isoprene in xylene at  $185^\circ$  gives  $2':6'\text{-dimethoxy-5-methyl-4'-n-amyl-1:2:3:6-tetrahydrodiphenyl-2-carboxylic acid}$  (I), m.p.  $115\text{--}115.5^\circ$  (or, in one experiment, an isomeride, m.p.  $133\text{--}134^\circ$ ). The  $\text{Me}$  ester, b.p.  $170^\circ/0.1\text{ mm.}$ , thereof with  $\text{S}$  at  $240\text{--}250^\circ$  followed by hydrolysis gives  $2':6'\text{-dimethoxy-5-methyl-4'-n-amylidiphenyl-2-carboxylic acid}$ , m.p.  $146^\circ$ , converted by  $48\%$   $\text{HBr--AcOH--Ac}_2\text{O}$  into the known  $3'\text{-hydroxy-4''-methyl-5'-n-amylidibenz-2-pyrone}$ , whence follows the orientation of (I). M.p. are corr. R. S. C.

**Symmetrical diaryls from diazotised amines. Reducing agents. II.** E. R. Atkinson, D. Holm-Hansen, A. D. Nevers, and S. A. Marino (*J. Amer. Chem. Soc.*, 1943, **65**, 476—477; cf. A., 1941, II, 170).— $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  with activated  $\text{Cu}$  powder (I) in  $\text{H}_2\text{O}$  at

5—10° gives *o*-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H (II) (54%) and diphenic acid (III) (32%), with (I) in dil. aq. NH<sub>3</sub> gives (III) (67—71%) and NH(C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H-*o*)<sub>2</sub> (10%), in warm 23*N*-HCO<sub>2</sub>H gives *o*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (IV) (<70%), with (I) in HCO<sub>2</sub>H gives BzOH (40%), (III) (10%), and tar, in warm EtOH gives (IV) (50—75%) and a little MeCHO, and with (I) in EtOH at 0° gives BzOH (50%), (II) (a little), and (*o*-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·N')<sub>2</sub> (very little). R. S. C.

**Tetracyanodimethylcyclopropane.** L. Ramberg and S. Wideqvist (*Arkiv Kemi, Min. Geol.*, 1941, **14**, B, No. 37, 13 pp.).—CHBr(CN)<sub>2</sub> and aq. COMe<sub>2</sub>—KI afford 1 : 1 : 2 : 2-tetracyano-3 : 3-dimethylcyclopropane (I), m.p. 209.5—210° (corr.). It is converted by boiling *N*-KOH into 1-carboxy-2-carbamyl-3 : 3-dimethylcyclopropane-1 : 2-dicarboxylimide (II), m.p. 197° (decomp.), also obtained by the action of alkali on 1 : 2-dicyano-3 : 3-dimethylcyclopropane-1 : 2-dicarboxylimide (III), m.p. 242°, prepared from *aa'*-dicyano-*ββ*-dimethylglutarimide and its *aa'*-Br<sub>2</sub>-derivative in boiling 40% AcOH. (II) is probably transformed by NaNO<sub>2</sub> in 25% H<sub>2</sub>SO<sub>4</sub> into the corresponding dicarboxylic acid. (I) is converted by KOH and conc. NH<sub>3</sub> in a sealed tube at 115° into a compound, m.p. 165°, which could not be obtained quite pure but is very probably caronic acid. Conc. HCl converts (I) or (III) into a compound, m.p. 265°, probably CMe<sub>2</sub><CH(CO<sub>2</sub>H)·CO>NH. (III) is also obtained from (I) and KOBz. H. W.

**Preparation of  $\alpha\beta$ -unsaturated aldehydes.** P. A. Plattner and L. M. Jampolsky (*Helv. Chim. Acta*, 1943, **26**, 687—694; cf. A., 1942, II, 102).—cycloHexanone-2-oxalic [2-ketohexahydrophenylglyoxylic] acid is converted by boiling Ac<sub>2</sub>O containing a little HBr—AcOH into the unstable 3 : 4 : 5 : 8-tetrahydrocoumaran-1 : 2-dione 3-enol acetate (I), m.p. 89—92°, which gives a yellow colour with C(NO<sub>2</sub>)<sub>4</sub> but no reaction with FeCl<sub>3</sub>. Hydrogenation (PtO<sub>2</sub> in EtOH) of (I) causes the uniform absorption of 3 H<sub>2</sub> and gives non-cryst. products. Partial hydrogenation (Pt in EtOH at 20°; H<sub>2</sub> = 1 mol.) of (I) gives hexahydrocoumaran-1 : 2-dione 3-enol acetate (II), m.p. 100—101°, or (H<sub>2</sub> = 2 mols.) 2-acetoxihexahydrocoumaran-1-one, m.p. 64—66°. (II) is hydrolysed (KOH—MeOH) to hexahydrocoumaran-1 : 2-dione, m.p. 99—101°, which when distilled in CO<sub>2</sub> under atm. pressure passes into  $\Delta^1$ -tetrahydrobenzaldehyde (oxime, m.p. 98—99°; semicarbazone, m.p. 213—216°). 2-Methylcyclohexanone is converted into 6-methyl-3 : 4 : 5 : 8-tetrahydrocoumaran-1 : 2-dione 2-enol acetate, m.p. 77—78°, hydrogenated and hydrolysed to 6-methylhexahydrocoumaran-1 : 2-dione, m.p. 107—108°, which when distilled over a free flame gives  $\Delta^2$ -tetrahydro-*m*-tolu-aldehyde (semicarbazone, m.p. 205—206°). M.p. are corr. H. W.

**Aromatic aldehydes.**—See B., 1943, II, 174.

**Stabilisation of aldehydes.**—See B., 1943, II, 174.

**Condensation of chloroacetophenone with ethanol- and diethanolamine and of chloroacetopyrocatechol with  $\beta$ -methoxyethylamine.** K. W. Brighton and E. E. Reid (*J. Amer. Chem. Soc.*, 1943, **65**, 479).—COPh·CH<sub>2</sub>Cl with NH<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·OH gives  $\omega$ - $\beta$ -hydroxyethyl-, m.p. 144°, and with NH([CH<sub>2</sub>]<sub>2</sub>·OH)<sub>2</sub> slowly gives  $\omega$ -di-( $\beta$ -hydroxyethyl)-aminoacetophenone, m.p. 44° (hydrochloride). 3 : 4 : 1-(OH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO·CH<sub>2</sub>Cl with OMe·[CH<sub>2</sub>]<sub>2</sub>·NH<sub>2</sub> gives  $\omega$ - $\beta$ -methoxyethyl-aminoacetopyrocatechol, m.p. 93° (hydrochloride, m.p. 186°). R. S. C.

**Preparation of phenylglyoxal.** B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1940, **14**, A, No. 9, 9 pp.).—CH<sub>2</sub>Bz·S·CH<sub>2</sub>R (R = CO<sub>2</sub>H, CH<sub>2</sub>·CO<sub>2</sub>H, or Ph) (cf. A., 1943, II, 183) with alkaline H<sub>2</sub>O<sub>2</sub> gives CH<sub>2</sub>Bz·SO·CH<sub>2</sub>R, which when distilled from dil. HCl + HgCl<sub>2</sub> yields BzCHO (I) and CH<sub>2</sub>R·S·HgCl. In absence of HgCl<sub>2</sub> mercaptans and additive products of (I) and the mercaptan are formed. The following are prepared:  $\beta$ -phenacylthiolpropionic, m.p. 46—49° (+H<sub>2</sub>O, m.p. 59—61°), and  $\beta$ -phenacylsulphinylpropionic, m.p. 121.5—122.5°, acids; compound 2(I), 2CH<sub>2</sub>Ph·SH, H<sub>2</sub>O, m.p. 69—70° (opaque; clear at 82°), volatile in steam; mercaptal, m.p. 150—151.5°, and semi-mercaptal, m.p. 106—108°, of (I) and SH·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H.  $\beta$ -Benzylsulphinylpropionic acid, m.p. 149—149.5° (decomp.), does not yield (I) with dil. HCl + HgCl<sub>2</sub>. M. H. M. A.

**Phenyl 2 : 4 : 6-trimethylbenzyl diketone.** R. P. Barnes and R. J. Brown (*J. Amer. Chem. Soc.*, 1943, **65**, 412—415).—Ph 2 : 4 : 6-trimethylbenzyl diketone (I), m.p. 55°, resembles CHPh<sub>2</sub>·CO·COPh rather than CH<sub>2</sub>Ph·CO·COMes (Mes = mesityl here and below) (cf. A., 1934, 410; 1935, 979), although the nuclear H are unusually reactive. MesCHO and COPh·CH<sub>2</sub>Br give a substance (poor yield), m.p. 137°, containing Br, but CHMes·CH·COPh and H<sub>2</sub>O<sub>2</sub> in MeOH—NaOH—H<sub>2</sub>O give  $\beta\gamma$ -epoxy- $\alpha$ -phenyl- $\gamma$ -mesitylpropan- $\alpha$ -one (80%), m.p. 73°, which with NaOH in hot MeOH gives (I). (I) gives no colour with FeCl<sub>3</sub> and is 100% ketonic (Kurt Meyer) in EtOH. With *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> it gives 2-phenyl-3-2' : 4' : 6'-trimethylbenzylquinoxaline, m.p. 118°. The structure of (I) is proved by cleavage by H<sub>2</sub>O<sub>2</sub>—aq. MeOH to BzOH and CH<sub>2</sub>Mes·CO<sub>2</sub>H. With Br in CHCl<sub>3</sub>, (I) gives Ph 3-bromo-2 : 4 : 6-trimethylbenzyl diketone (II), m.p. 72° [derived quinoxaline (III), m.p. 161°], converted by H<sub>2</sub>O<sub>2</sub> etc. into BzOH and 2 : 4 : 6 : 3 : 1-C<sub>6</sub>HMe<sub>3</sub>Br·CO<sub>2</sub>H and giving with boiling Ac<sub>2</sub>O—KOAc (not AcOH—KOAc) the enol acetate (IV), m.p. 107°,

stable to Br—CHCl<sub>3</sub>. Cold, conc. H<sub>2</sub>SO<sub>4</sub> hydrolyses (IV) to the enolic form (V), m.p. 147°, of (II) [which also yields (IV) and (III)]; in boiling EtOH, (V) yields (II) and it reacts with H<sub>2</sub>O<sub>2</sub> as does (II). Dissolving (II) in H<sub>2</sub>SO<sub>4</sub> and pouring the solution on to ice gives (V). In Et<sub>2</sub>O, (V) and Br yield an oily compound, C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>Br<sub>2</sub>, which with KI—COMe<sub>2</sub> gives I and (II). R. S. C.

**Synthesis of 2-ketocyclohexylsuccinic acid and related substances.**  
**II. Syntheses involving cyclohexanone.** E. H. Charlesworth, J. A. McRae, and H. M. MacFarlane (*Canad. J. Res.*, 1943, **21**, B, 55—64).—Et cyclohexanone-2-carboxylate (I) is converted by the successive actions of Na and CH<sub>2</sub>Br·CO<sub>2</sub>Et in boiling C<sub>6</sub>H<sub>6</sub> into the 2-carboxylate-2-acetate, b.p. 195—210°/45 mm., hydrolysed and decarboxylated by boiling conc. HCl to 2-ketocyclohexylacetic acid, m.p. 75—78° (phenylhydrazine, m.p. 162—163°). (I), CHMeBr·CO<sub>2</sub>Et, and NaOEt in boiling EtOH afford Et  $\alpha$ -2-keto-1-carbethoxycyclohexylpropionate, b.p. 180—190°/17 mm., whence (boiling conc. HCl)  $\alpha$ -2-ketocyclohexylpropionic acid. Similar condensation of (I) with CH<sub>2</sub>Ph·CHBr·CO<sub>2</sub>Et leads to CH<sub>2</sub>Ph·CH(OH)·CO<sub>2</sub>Et, converted by conc. HCl into CHPh·CH·CO<sub>2</sub>H. Attempts to condense (I) with CHBr(CO<sub>2</sub>Et)<sub>2</sub> and Na in C<sub>6</sub>H<sub>6</sub> lead to [CH(CO<sub>2</sub>Et)<sub>2</sub>]<sub>2</sub> whereas with NaOEt in EtOH the product appears to be [C(CO<sub>2</sub>Et)<sub>2</sub>]<sub>2</sub>, m.p. 54—55°. (I) and CO<sub>2</sub>Et·CHBr·CH<sub>2</sub>·CO<sub>2</sub>Et (II) in EtOH—NaOEt give a product, b.p. 237°/10 mm., hydrolysed to an acid, m.p. 102—103° (not 2-ketocyclohexylsuccinic acid). cycloHexanone (III), CH<sub>2</sub>Br·CO<sub>2</sub>Et, and Zn in boiling C<sub>6</sub>H<sub>6</sub> give Et 1-hydroxycyclohexylacetate, b.p. 143—146°/37 mm., transformed by boiling conc. HCl into cyclohexanolaceto- $\gamma$ -lactone, b.p. 152—156°/28 mm. cycloHexanol- $\alpha$ -propio- $\gamma$ -lactone, b.p. 150°/21 mm., is obtained similarly. The Reformatsky reaction could not be achieved with (III) and CHBr(CO<sub>2</sub>Et)<sub>2</sub> or (II). H. W.

**Indanone ring-closure of unsymmetrical  $\beta\beta$ -diarylpropionic acids.** C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 422—424).—CHPh·CH·CO<sub>2</sub>H, PhBr, and AlCl<sub>3</sub> at 20° give, after esterification, Me  $\beta$ -phenyl- $\beta$ -p-bromophenylpropionate, b.p. 220—225°/24 mm., and thence the acid, m.p. 107—108°, which with PCl<sub>5</sub>—CS<sub>2</sub> (later warm) and then AlCl<sub>3</sub>—CS<sub>2</sub> at 10—15° (later room temp.) gives 3-p-bromophenylindanone (I), m.p. 59—60°. With CrO<sub>3</sub> this gives *o*-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·CO·C<sub>6</sub>H<sub>4</sub>Br-*p*, m.p. 172—173°, proving the structure of (I) (cf. Kohler *et al.*, A., 1910, i, 562; Waldmann *et al.*, A., 1930, 600). The dibromo-3-phenylindanone of Kohler *et al.* (*loc. cit.*) is the 2 : 4'-Br<sub>2</sub>-compound, since it is reduced to (I) by MgMeI in boiling Et<sub>2</sub>O. R. S. C.

**Apparently anomalous bromination in the polyphenylindene series.**

C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 419—422).—2 : 3-Diphenylindene (I) and Br (1 mol.) in AcOH containing (very slowly without) a little HBr give 3-phenyl-2-p-bromophenylindene (II), m.p. 145—146°, the structure of which is proved by oxidation (CrO<sub>3</sub>) to *p*-C<sub>6</sub>H<sub>4</sub>Br·CO<sub>2</sub>H (III) and *o*-C<sub>6</sub>H<sub>4</sub>Bz·CO<sub>2</sub>H and by the following synthesis: *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O with *p*-C<sub>6</sub>H<sub>4</sub>Br·CH<sub>2</sub>·CO<sub>2</sub>H (IV) gives  $\alpha$ -p-bromobenzylidenephthalide, m.p. 154—155°, which with MgPhBr gives (II). Similarly, the compound, m.p. 200—201°, obtained from 2 : 3 : 5 : 6-tetraphenylindene (V) (A., 1943, II, 35) is 3 : 5 : 6-triphenyl-2-p-bromophenylindene, since with CrO<sub>3</sub> it yields (III) and 4 : 5 : 2 : 1-C<sub>6</sub>H<sub>2</sub>Ph<sub>2</sub>Bz·CO<sub>2</sub>H. With an excess of Br, (I) gives 6-bromo-3-phenyl-2-p-bromophenylindene, m.p. 201—202°, which with KMnO<sub>4</sub> in COMe<sub>2</sub> gives 4 : 5'-dibromo-2'-benzoylbenzil, m.p. 140—141°, and thence (H<sub>2</sub>O<sub>2</sub>—alkali) (III) and 2 : 5 : 1-C<sub>6</sub>H<sub>3</sub>BzBr·CO<sub>2</sub>H. 2 : 3 : 4 : 7-Tetraphenylindene (VI), m.p. 204—205°, and Br give a mixture, including 6- (or 5-)bromo-3 : 4 : 7-triphenyl-2-p-bromophenylindene (VII), m.p. 254—255°, the location of one Br being proved as follows: 3 : 6 : 1 : 2-C<sub>6</sub>H<sub>2</sub>Ph<sub>2</sub>(CO)<sub>2</sub>O and (IV) give 3 : 6-diphenyl- $\alpha$ -p-bromobenzylidenephthalide, m.p. 213—214°, converted by MgPhBr into 3 : 4 : 7-triphenyl-2-p-bromophenylindene, m.p. 257—258°, which with Br gives (VII) and with CrO<sub>3</sub> gives (III). The appropriate substituted *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O with CH<sub>2</sub>Ph·CO<sub>2</sub>H gives 4 : 5-, m.p. 212—213°, and 3 : 6-diphenyl-, m.p. 166—167°, 4 : 5-diphenyl-3 : 6-dimethyl-, m.p. 232—233° (also obtained from the H<sub>2</sub>-anhydride at >290°), and 3 : 4 : 5 : 6-tetraphenyl-, m.p. 338—340°, - $\alpha$ -benzylidenephthalide and thence (MgPhBr) (V), (VI), 2 : 3 : 4 : 7-tetraphenyl-5 : 6-dimethyl-, m.p. 234—235°, and 2 : 3 : 4 : 5 : 6 : 7-hexaphenylindene, m.p. 279—280°, respectively. Identity of (V) is confirmed by conversion by MgPhBr into the known carbinol. The need for HBr during the brominations is explained by a mechanism involving quinonoid ions, which involves location of a Br at C<sub>6</sub> of (VII). R. S. C.

**Modification of the Ullmann synthesis of fluorene derivatives.** W. C. Lothrop and P. A. Goodwin (*J. Amer. Chem. Soc.*, 1943, **65**, 363—367).—Adding 2-methyl-4 : 5-benz-1 : 3-oxaz-6-one (I) in C<sub>6</sub>H<sub>6</sub> to Et<sub>2</sub>O—MgPhBr gives *o*-NHAc·C<sub>6</sub>H<sub>4</sub>·CPh<sub>2</sub>·OH (23%), m.p. 197—198° (lit. 192°), identified by hydrolysis by HCl—EtOH to *o*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CPh<sub>2</sub>·OH, m.p. 119° (lit. 121.5°), converted by Ac<sub>2</sub>O—NaOAc into 6 : 6-diphenyl-2-methyl-4 : 5-benz-1 : 3-oxazine, m.p. 137—139° (lit. 135—137°). The reverse addition gives *o*-NHAc·C<sub>6</sub>H<sub>4</sub>·COPh (33%), m.p. 88° (lit. 89°), and thence (conc. HCl—EtOH) *o*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·COPh. Adding *o*-C<sub>6</sub>H<sub>4</sub>Me·MgBr to (I) gives similarly 2'-acetamido- (43%), m.p. 104°, and thence 2'-amino-

2-methylbenzophenone, m.p. 84°, which with  $\text{NaNO}_2$ -5N-HCl gives 1-methylfluoren-9-one (II) (49%), m.p. 98° (identified by oxidation by  $\text{KMnO}_4$  to the 1-carboxylic acid), and a little 2'-hydroxy-2-methylbenzophenone, m.p. 65–67°. Boiling 47% HI and red P reduce (II) slowly to 1-methylfluorene, m.p. 87°.  $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$  gives an oil, hydrolysed to 2'-amino-3-methylbenzophenone (10% over-all), m.p. 57°, which yields a trace of 2-methylfluorenone. Adding  $1\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$  to (I) gives  $o\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\alpha\text{-C}_{10}\text{H}_7$  ketone (III) (47%), m.p. 125°; the reverse addition gives less (III) and some  $o\text{-acetamido-}$ , m.p. 209–211°, hydrolysed to  $o\text{-amino-phenyldi-}a\text{-naphthylcarbinol}$ , m.p. 206° (decomp.). (III) yields, as above,  $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_{10}\text{H}_7$ ,  $1:2$ -benzfluoren-9-one, and chrysfluorene. Adding  $2:1\text{-C}_{10}\text{H}_6\cdot\text{Me}\cdot\text{MgBr}$  to (I) gives  $o\text{-acetamido-}$  (34%), m.p. 132°, and thence  $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot 2\text{-methyl-1-naphthyl ketone}$ , m.p. 114°, and 6-methyl-7-benzanthrone.  $2\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$  leads to an oil, which yields  $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\beta\text{-C}_{10}\text{H}_7$  ketone (8.3%), m.p. 106°, and thence traces of  $3:4$ -benzfluorenone.  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  and  $1:3:4\text{-C}_6\text{H}_3\text{Me}_2\cdot\text{MgI}$  with (I) give only oils. Adding  $\text{MgPhBr}$  to 2-methyl-4:5-2':3'-naphth-1:3-oxaz-6-one (IV) gives Ph 2-acetamido (39%), m.p. 141–145°, and thence Ph 2-amino-3-naphthyl ketone (V), m.p. 114°; some diphenyl-2-acetamido-3-naphthylcarbinol, m.p. 226° (decomp.), is also formed. Ring-closure of (V) as above yields 2:3-benzfluorenone (13%) and a little Ph 2-hydroxy-3-naphthyl ketone, m.p. 156°.  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  and (IV) give only a small yield of  $\alpha\gamma$ -diphenyl- $\beta$ -2-acetamido-3-naphthylpropan- $\beta$ -ol, m.p. 181°.  $2\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$  and (IV) give  $\beta\text{-C}_{10}\text{H}_7$ , 2-acetamido-, m.p. 169°, and thence 2-amino-3-naphthyl ketone (4% over-all), m.p. 154–156°, which by diazotisation etc. yields 2:3:5:6-dibenzfluoren-9-one, m.p. 185° (resists reduction), and a little  $\beta\text{-C}_{10}\text{H}_7$ , 2-hydroxy-3-naphthyl ketone, m.p. 139°.

R. S. C.

**Polynitro-compounds of fluorene.** F. E. Ray and W. C. Francis (*J. Org. Chem.*, 1943, 8, 52–59).—2:2'-Dinitrodiphenyl-6-carboxylic acid is converted by conc.  $\text{H}_2\text{SO}_4$  at  $190^\circ \pm 5^\circ$  into 4:5-dinitrofluorenone (I), m.p. 273.5°. The substance, m.p. 243° [oxime, m.p. 265°; phenylhydrazone, new m.p. 252–253° (decomp.)], thus described by Schmidt *et al.* (A., 1906, i, 27), is the 2:5-( $\text{NO}_2$ )<sub>2</sub>-compound; it is formed with 4:6'-dinitrodiphenic acid, new m.p. 306–307°, by the oxidation of 2:5-dinitrophenanthraquinone by  $\text{KMnO}_4$  in the presence of alkali. 2:4:7-Trinitrofluorenone (II), m.p. 175.5°, is obtained by nitration of 2:5- and 2:7-dinitrofluorenone (cf. Bell, A., 1928, 1010); the compound is identical with the "2:6:7- (or 2:3:7)-trinitrofluorenone" of Schmidt *et al.* (*loc. cit.*). It is very resistant to oxidation by acid  $\text{KMnO}_4$ . 2:4:5:7-Tetranitrofluorenone, m.p. 252–253°, is obtained from (I) or (II) and a mixture of boiling fuming  $\text{HNO}_3$  ( $d$  1.59–1.60) and conc.  $\text{H}_2\text{SO}_4$ .

H. W.

1:2:5:6-Dibenzfluorenone.—See B., 1943, II, 174.

**Preparation of derivatives of chrysene by the Robinson-Mannich base synthesis of unsaturated ketones.** A. L. Wilds and C. H. Shunk (*J. Amer. Chem. Soc.*, 1943, 65, 469–475).—The hygroscopic methiodide from pure  $\text{NEt}_2\cdot[\text{CH}_2]_2\cdot\text{COMe}$  (I) (modified prep. from paraformaldehyde,  $\text{COMe}_2$ , and  $\text{NH}_4\text{Et}_2\text{HCl}$  in EtOH) with Me 1-keto-1:2:3:4-tetrahydrophenanthrene-2-carboxylate (II) and NaOMe (1 mol.) in  $\text{MeOH}\text{-C}_6\text{H}_6$  gives 92% of Me 1-keto-2- $\gamma$ -keton-butyl-1:2:3:4-tetrahydrophenanthrene-2-carboxylate (III), m.p. 145–145.5°; owing to its content of  $\delta$ -diethylamino- $\gamma$ -diethylamino-methylbutan- $\beta$ -one (IV), b.p. 92–92.5°/0.4 mm. (prep. described), crude (I) gives much lower yields of (III). The dimethiodide of (IV) with (II) gives Me 1-keto-2- $\gamma$ -keto- $\beta$ -methylene-n-butyl-1:2:3:4-tetrahydrophenanthrene-2-carboxylate (V) (72%), m.p. 157.5–158.5°. In boiling  $\text{KOH}\text{-MeOH}\text{-N}_2$  or conc.  $\text{HCl}\text{-AcOH}\text{-N}_2$ , (III) gives 5-keto-1:2:2a:3:4:5-hexahydrochrysene (VI) (90 or 84%), m.p. 188–188.5° [oxime, sinters 218°, m.p. 220–222° (decomp.)] [and a trace of an acid, m.p. 232–234° (gas)], but in boiling NaOMe-MeOH- $\text{N}_2$  gives Me 5-keto-1:2:2a:3:4:5-hexahydrochrysene-2a-carboxylate (79%), m.p. 178.5–179.5°, which is indifferent to hot  $\text{HCl}\text{-AcOH}$  but in  $\text{KOH}\text{-MeOH}$  yields (VI). Pd-C- $\text{N}_2$  dehydrogenates (VI) at 280–300° to chrysene (78%) and 5-hydroxychrysene (18%), m.p. 271–273° (acetate, m.p. 201–202°; Me ether, m.p. 147.5–148.5°; no  $\text{FeCl}_3$  colour), the latter being the main product (83% + a trace of a neutral substance, m.p. 135–155°) obtained by Pd-C in xylene- $\text{N}_2$ . When treated with  $\text{MgMeI}\text{-Et}_2\text{O}\text{-C}_6\text{H}_6$  and then aq.  $\text{NH}_4\text{Cl}$  and finally Pd-C at 300–320°, (VI) gives 5-methylchrysene (76%). In conc.  $\text{HCl}\text{-AcOH}\text{-N}_2$ , (V) gives 5-acetoxy- (VII) (76–83%), m.p. 167–168°, and thence (conc.  $\text{HCl}\text{-EtOH}\text{-N}_2$ ) 5-hydroxy-4-methyl-1:2-dihydrochrysene (VIII), m.p. 159–160°;  $\text{KOH}\text{-MeOH}$  yields >43%. With Pd-C- $\text{N}_2$  at 200–250° and then boiling  $\text{Ac}_2\text{O}$ , (VII) gives 5-acetoxy-, di- (? tri-)morphic, m.p. 185–187°, and thence 5-hydroxy-4-methylchrysene, m.p. 287–288° (vac.).  $\text{H}_2\text{-Pd-C}$  in dioxan converts (V) into mixed Me 1-keto-2- $\gamma$ -keto- $\beta$ -methyl-n-butyl-1:2:3:4-tetrahydrophenanthrene-2-carboxylates, form, m.p. 123.5–124.5°, and thence ( $\text{KOH}\text{-MeOH}$ ) mixed 5-keto-4-methyl-1:2:2a:3:4:5-hexahydrochrysenes (IX), form, m.p. 189–189.5° [oxime, m.p. ~252–254° (decomp.)], which is dehydrogenated as above to (VIII) and with  $\text{Zn-Hg-HCl}$  and then Pd-C yields 4-methylchrysene, m.p. 229.5–230°.

R. S. C.

**Oximation of juglone.** H. Goldstein and P. Grandjean (*Helv. Chim. Acta*, 1943, 26, 181–185).—Oximation of 5-hydroxy-1:4-

naphthaquinone (juglone) (I) occurs in position 1. 5-Hydroxy-1:4-naphthaquinone-1-oxime, decomp. 203° [lit. m.p. 187° (decomp.)], is reduced and then benzoylated to 4:1:8-NHBz· $\text{C}_{10}\text{H}_5(\text{OBz})_2$ , m.p. 247°, prepared for comparison from 4-benzeneazo-1:8-dihydroxynaphthalene. 4-Benzamido-, m.p. 233°, and 2-benzamido-, m.p. 213°, 1:5-dibenzoyloxynaphthalene are described. (I) is obtained by oxidation of 1:5:4-(OH)<sub>2</sub>· $\text{C}_{10}\text{H}_5\cdot\text{NH}_2$ . M.p. are corr.

H. W.

**Naphthazarin.** H. E. Fierz-David and W. Stockar (*Helv. Chim. Acta*, 1943, 26, 92–98).—Naphthazarin (I) is obtained in 59% yield by the addition of a solution of S (7 g.) in 66% oleum (120 g.) to 1:5- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$  in  $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$  (400 g.) at  $>40^\circ$  and is purified by sublimation at 170–180°/vac. Addition of  $\text{H}_3\text{BO}_3$  does not improve the yield. Reduction of 1:5- or 1:8- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$  by  $\text{NH}_2\text{Ph}$  in conc.  $\text{H}_2\text{SO}_4$  gives (I) in only 22% or 11.5% yield respectively. (I) condenses with  $\text{NH}_2\text{Ar}$  usually at room temp. to 2-aryl-amino-5:8-dihydroxy-1:4-naphthaquinones; products are described from  $\text{NH}_2\text{Ph}$ ,  $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ ,  $o$ - and  $m$ -toluidine,  $m$ - and  $p$ -xylidine, and  $m$ - and  $o$ - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ .  $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ ,  $\alpha$ - and  $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ ,  $m$ - and  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  also condense. 2-Anilino-5:8-dihydroxy-1:4-naphthaquinone is sulphonated to a marine-blue dye. A second arylamino-residue is introduced if (I) is heated for some time with an excess of base but the products are sol. with great difficulty.

H. W.

**Oximation of 2-hydroxy- and 2-anilino-1:4-naphthaquinone.** H. Goldstein and P. Grandjean (*Helv. Chim. Acta*, 1943, 26, 468–475).—Oximation of 2-hydroxy-1:4-naphthaquinone in acid or alkaline medium gives 2-hydroxy-1:4-naphthaquinone-1-oxime (I), m.p. ~195° (decomp.) (lit. decomp. 180°). It is reduced to 1:2:4- $\text{NH}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})_2$  [ $\text{Ac}_3$  derivative (II), m.p. 155.5°]. 1:3- $\text{C}_{10}\text{H}_8(\text{OH})_2$  is converted by  $\text{CH}_2\text{Bu}^o\cdot\text{O}\cdot\text{NO}$  in  $\text{EtOH}\text{-KOH}$  at  $0^\circ$  into 4:1:3- $\text{NO}\cdot\text{C}_{10}\text{H}_5(\text{OH})_2$  identical with (I) and yielding (II) when reduced and acetylated, thus proving the structure of (I). 2-Methoxy-1:4-naphthaquinone can be obtained directly by heating 1:2- $\text{NO}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$  with  $\text{MeOH}\text{-conc. H}_2\text{SO}_4$ . 2-Anilino-1:4-naphthaquinone does not react with  $\text{NH}_2\text{OH}$  in acid solution but in alkaline medium affords the 1-oxime (III), m.p. 222° (decomp.). This is reduced to 3:4:1-NHPh· $\text{C}_{10}\text{H}_5(\text{NH}_2)\cdot\text{OH}$ , the ON-Bz<sub>2</sub> derivative, m.p. 235°, of which with boiling  $\text{AcOH}$  gives 5-benzoyloxy-2:3-diphenyl- $\alpha$ -naphthiminazole (IV), m.p. 181°, thus establishing the vicinal position of NHPh and :N·OH in (III). (IV) is converted by successive treatments with  $\text{KOH}\text{-EtOH}$  and  $\text{Me}_2\text{SO}_4$  into 5-methoxy-2:3-diphenyl- $\alpha$ -naphthiminazole (V), m.p. 162°. 1:4- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\text{Ph}$  is converted by the successive action of  $\text{SnCl}_2$  and aq.  $\text{HCl}$  into 4-amino-3-anilino-1-methoxynaphthalene, m.p. 182° (decomp.); the Bz derivative, m.p. 195°, of this is converted into (V) by boiling glacial  $\text{AcOH}$ , thus confirming the structure of (IV). M.p. are corr.

H. W.

2-Methyl-3-phytyl-1:4-naphthaquinone.—See B., 1943, III, 136.

**Celastrol.** IV. O. Gisvold (*J. Amer. Pharm. Assoc.*, 1942, 31, 529–532; cf. A., 1941, II, 18).—Celastrol (I) with  $\text{AcOH}\text{-O}_3$  is degraded to a CO-acid, m.p. 166–167°, [ $\alpha$ ] +22.1° in EtOH (2:4-dinitrophenylhydrazones,  $\text{C}_{25}\text{H}_{32}\text{O}_7\text{N}_4$ , m.p. 192°). Acetylation (Thiele) of (I) and methylcelastrol gives colourless, abnormal triacetates,  $\text{C}_{28}\text{H}_{38}\text{O}_7$ , m.p. 100–101°, and  $\text{C}_{29}\text{H}_{40}\text{O}_7$ , respectively. (I) is reduced ( $\text{Pt-H}_2$ ) to dihydrocelastrol, m.p. 177°, which readily oxidises to (I). (I) is 8-hydroxy-3-methyl-4-homohydrogeranyl- (or -hydrogeranyl-) 1:2-naphthaquinone.

F. O. H.

## IV.—STEROLS AND STEROID SAPOGENINS.

**Sensitive colour reaction for steroids.** M. C. Nath (*Ann. Biochem. Exp. Med.*, 1942, 2, 83–86).—When conc.  $\text{H}_2\text{SO}_4$  is poured down the side of a test-tube containing a solution of a steroid in glacial  $\text{AcOH}$  containing a drop of 1%  $\text{Hg}(\text{OAc})_2$  in glacial  $\text{AcOH}$ , a brown, red, or violet ring develops at the junction of the two layers with a blue or green ring above it. Variations observed with different concns. of the reagents are described.

P. C. W.

**Colour reaction of steroids in relation to their structures.** M. C. Nath and M. K. Chakraborty (*Ann. Biochem. Exp. Med.*, 1942, 2, 73–82).—An attempt is made to correlate the location of double linkings in steroids with the colours developed by particular reagents. It is suggested that a  $\Delta^4:5$  linking (actual or potential) is responsible for the development of red or carmine and a  $\Delta^7:8$  linking for the blue colour in Rosenheim's, Kohlenberg's, and Rosenheim and Callow's reactions. The relation between structure and the absorption bands found during the colour development is discussed.

P. C. W.

**Preparation of cholesteryl *p*-aminobenzoate.** D. Kritchevsky (*J. Amer. Chem. Soc.*, 1943, 65, 480).—Cholesteryl *p*-nitrobenzoate, m.p. 190.5–191.5°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> –6.97° in  $\text{CHCl}_3$ , with Fe filings in boiling  $\text{AcOH}$  gives the *p*-aminobenzoate, m.p. 237.8–238.8°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +3.68° in  $\text{CHCl}_3$ , hydrolysed by hot  $\text{NaOH}\text{-EtOH}$ .

R. S. C.

**Scymnol.** W. Bergmann and W. T. Pace (*J. Amer. Chem. Soc.*, 1943, 65, 477–478).—Location of OH at  $\text{C}_{13}$  (cf. Ashikari, A., 1939, III, 692) is confirmed. Scymnol tetra-acetate, m.p. 145.5–

147°, with  $\text{CrO}_3$ -AcOH at 90° gives (after hydrolysis) cholic and then 3:7:12-triketocholic acid (I). Tschesche's products (A., 1932, 268) were impure. Scymnoltriketo-acid (Windaus, A., 1930, 1039) with conc.  $\text{HCl}$ -AcOH gives the *chlorohydrin*,  $\text{C}_{27}\text{H}_{48}\text{O}_8\text{Cl}$ , m.p. 225—227°, which with  $\text{CrO}_3$ -AcOH at 80° yields (I).

R. S. C.

**Oxidative degradation of *i*-stigmasteryl methyl ether.** B. Riegel, E. W. Meyer, and J. Beiswanger (*J. Amer. Chem. Soc.*, 1943, 65, 325—328).—Formation of *i*-ethers is used to protect the OH at  $\text{C}_{13}$  of sterols. *i*-Stigmasteryl Me ether (from stigmasteryl in 77% yield) with  $\text{O}_3$  in  $\text{CHCl}_3$  at 0° and then  $\text{H}_2\text{O}_2$  gives 6-methoxy-*i*-bisnorcholenic acid (I),  $+\text{H}_2\text{O}$  and anhyd., m.p. 174.8—176.3°,  $[\alpha]_D^{25} +17^\circ$  in  $\text{CHCl}_3$ , which gives gums when rearranged. Me 3-*p*-toluenesulphonyloxy- $\Delta^5$ -bisnorcholenate (II), m.p. 133—134°, and KOAc in boiling MeOH give Me 6-methoxy-*i*-bisnorcholenate (III) (98%), m.p. 72.0—72.8°,  $[\alpha]_D^{25} +37.3^\circ$  in  $\text{CHCl}_3$ , converted by KOH-MeOH into (I) having m.p. 168—171° and  $[\alpha]_D^{25} +33^\circ$  in  $\text{CHCl}_3$ . With a little  $\text{H}_2\text{SO}_4$  in boiling MeOH, (III) gives Me 3-methoxy- $\Delta^5$ -bisnorcholenate (IV), m.p. 117—118°,  $[\alpha]_D^{25} -63.3^\circ$  in  $\text{CHCl}_3$ , which is also obtained by boiling (II) in MeOH and by rearranging the crude Me ester from either "form" of (I). Boiling KOH-MeOH hydrolyses (IV) to the acid, m.p. 199—202°,  $[\alpha]_D^{25} -77.8^\circ$  in  $\text{CHCl}_3$ . With boiling  $\text{Zn}(\text{OAc})_2$ - $\text{Ac}_2\text{O}$ -AcOH, (III) gives Me 3-acetoxy- $\Delta^5$ -bisnorcholenate. M.p. are corr.

R. S. C.

**Preparation of deoxycholic acid from cholic acid.** G. A. D. Haslewood (*Biochem. J.*, 1943, 37, 109—112).—A more detailed account of work previously abstracted (A., 1942, II, 365). 3:12-Dihydroxy-7-ketocholic acid, m.p.  $\sim 83^\circ$ , and its Et ester, m.p. 160—161°, are new.

R. L. E.

**Preparation of deoxycholic acid from cholic acid.** A. W. Schneider and W. M. Hoehn (*J. Amer. Chem. Soc.*, 1943, 65, 485).—Oxidation of cholic acid or its Me ester by  $\text{CrO}_3$  in AcOH or AcOH- $\text{C}_6\text{H}_6$  and heating (170—200°) the semicarbazones or hydrazones of the products with KOH- or NaOH-MeOH gives deoxycholic acid,  $[\alpha]_D^{25} +57^\circ \pm 1^\circ$  in MeOH, which is similarly obtained from Me 7:12-dihydroxy-3-benzoyloxycholesterol when the sol. (MeOH) semicarbazone of the oxidation product is used.

R. S. C.

**Constitution of cafestol.** A. Wettstein and K. Miescher (*Helv. Chim. Acta*, 1943, 26, 631—641; see also A., 1943, II, 203).—*t*-Dehydroandrosterone with piperonal and  $m\text{-NO}_2\text{-C}_6\text{H}_4\text{-CHO}$  in an alkaline medium gives 16-piperonylidene-, m.p. 242—243°, and 16-*m*-nitrobenzylidene- $\Delta^5$ -androsten-3 $\alpha$ -ol-17-one, m.p. 248.5—250°, respectively. 16-*m*-Nitrobenzylidene- $\Delta^5$ -androsterone, m.p. 189—190°, and -*estrone* Me ether, m.p. 187—188°, are similarly prepared. M.p. are corr.

H. W.

**Saccharides of deoxycorticosterone.**—See A., 1943, II, 156.

**Alengol.**—See A., 1943, II, 211.

**Steroids. VII. Compounds related to 6-methyl-11-deoxycorticosterone.** M. Ehrenstein (*J. Org. Chem.*, 1943, 8, 83—94).— $\Delta^5$ -Pregnene-3( $\beta$ ):21-diol-20-one 21-acetate is converted by  $\text{Al}(\text{OPr}^i)_3$  in boiling  $\text{Pr}^i\text{OH}$  followed by hydrolysis and treatment with  $\text{COMe}_2$  and anhyd.  $\text{CuSO}_4$  into  $\Delta^5$ -pregnene-3( $\beta$ ):20:21-triol 20:21- $\text{COMe}_2$  ether, m.p. 175°,  $[\alpha]_D^{25} -46.5^\circ$  in  $\text{COMe}_2$ , which is hydrolysed by EtOH-aq. AcOH to  $\Delta^5$ -pregnene-3( $\beta$ ):20:21-triol, m.p. 222—229°,  $[\alpha]_D^{25} -54.0^\circ$  in MeOH. This with  $\text{BzO}_2\text{H}$  in  $\text{CHCl}_3$  gives 5:6-oxido-pregnane-3( $\beta$ ):20:21-triol (I), m.p. 221—223°,  $[\alpha]_D^{25} -63.5^\circ$  in  $\text{COMe}_2$ . (I) is converted by  $\text{MgMeBr}$  in  $\text{Et}_2\text{O}$ -PhOMe ultimately at 130° into 6-methylpregnane-3( $\beta$ ):5:20:21-tetraol, m.p. 229—230° (decomp.),  $[\alpha]_D^{25} -24.0^\circ$  in MeOH, partly acetylated by  $\text{Ac}_2\text{O}$  in cold  $\text{C}_6\text{H}_6$  to the 21-monoacetate (II), m.p. 177.5—180°,  $[\alpha]_D^{25} +15.0^\circ$  in MeOH, with some 3:21-diacetate (III), m.p. 185—187°. (II) is oxidised by  $\text{CrO}_3$  in AcOH to 6-methylpregnane-5:20:21-triol-3-one 20:21-diacetate, m.p. 205—210°, converted by  $\text{HCl}$  in  $\text{CHCl}_3$  into resinous 6-methyl- $\Delta^4$ -pregnene-20:21-diol-3-one diacetate. (III) is oxidised by  $\text{CrO}_3$  in AcOH to the non-cryst. 6-methylpregnane-3( $\beta$ ):5:21-triol-20-one 3:21-diacetate.

H. W.

**Steroids and sex hormones. LXXXIV. 17( $\alpha$ )-Hydroxy-20-ketocompounds of the pregnene and allopregnane series.** M. W. Goldberg, R. Aeschbacher, and E. Hardegger (*Helv. Chim. Acta*, 1943, 26, 680—686; cf. Staveland, A., 1942, II, 147).—17-Acetylenyl- $\Delta^5$ -androsterone-3( $\beta$ ):17( $\alpha$ )-diol is converted by ( $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}$ ) $_2\text{Hg}$  in boiling 96% EtOH with subsequent treatment of the product with  $\text{H}_2\text{S}$  and then 2N-KOH into  $\Delta^5$ -pregnene-3( $\beta$ ):17( $\alpha$ )-diol-20-one (I), hexagonal leaflets or long needles, m.p. 190—191°,  $[\alpha]_D -83.6^\circ \pm 3^\circ$  and  $-87.9^\circ \pm 3^\circ$  in dioxan, respectively [oxime, m.p.  $\sim 255$ —260°; 3-monoacetate, m.p. 186—188°, and its oxime, m.p. 235—240° (decomp.)]. 17-Acetylenyl- $\Delta^5$ -androsterone-3( $\beta$ ):17( $\alpha$ )-diol diacetate is transformed similarly into the diacetate, m.p. 194—195°,  $[\alpha]_D -54.4^\circ \pm 3^\circ$  in dioxan, of (I), also obtained by protracted treatment of (I) with  $\text{Ac}_2\text{O}$ - $\text{C}_6\text{H}_5\text{N}$  at 105°. (I) is apparently transformed by  $\text{Al}(\text{OBu}^t)_3$  in  $\text{C}_6\text{H}_6$ - $\text{COMe}_2$  into (mainly) 3( $\beta$ ):17( $\alpha$ )-dihydroxy-17 $\alpha$ -methyl- $\Delta^5$ -D-homoandrosten-17-one, m.p. 176—178°. 17-Acetylenyltestosterone is converted [as for (I)] into  $\Delta^4$ -pregnen-17( $\alpha$ )-ol-3:20-dione, m.p. 192—193°,  $[\alpha]_D +64.4^\circ \pm 3^\circ$  in dioxan, almost quantitatively isomerised by activated  $\text{Al}_2\text{O}_3$  to 17( $\alpha$ )-hydroxy-17 $\alpha$ -methyl- $\Delta^4$ -D-homoandrosterone-3:17-dione, m.p. 181—184°, and

converted by KOH-MeOH into 17( $\alpha$ )-hydroxy-17 $\alpha$ -methyl- $\Delta^4$ -D-homoandrosterone-3:17-dione with (predominantly) non-investigated acidic products. 17-Acetylenylandrosterone-3( $\beta$ ):17( $\alpha$ )-diol yields 3( $\beta$ ):17( $\alpha$ )-dihydroxyallopregnane-20-one, m.p. 208—210°,  $[\alpha]_D -22.9^\circ \pm 2^\circ$  in dioxan [3-monoacetate, m.p. 139—142° (lit. 190—192°)]. M.p. are corr.

H. W.

**Constituents of the adrenal cortex and related substances. LIX.  $\Delta^4$ -Pregnen-21-ol-3:12:20-trione and -12( $\beta$ ):21-diol-3:20-dione.** H. G. Fuchs and T. Reichstein (*Helv. Chim. Acta*, 1943, 26, 511—530).—Diacetylatideoxycholic acid is converted by successive treatment with  $\text{SOCl}_2$  and  $\text{CH}_2\text{N}_2$  into non-cryst. 21-diazopregnane-3( $\alpha$ ):12( $\beta$ )-diol-20-one diacetate (I), hydrolysed by KOH-MeOH at room temp. to the corresponding diol (II). In AcOH at 100° (II) passes into pregnane-3( $\alpha$ ):12( $\beta$ ):21-triol-20-one 21-monoacetate (III), m.p. 149.5—150.5°,  $[\alpha]_D^{18} +139.7^\circ \pm 4^\circ$  in  $\text{COMe}_2$  (also  $+1\text{H}_2\text{O}$ ), which with  $\text{Ac}_2\text{O}$  and  $\text{C}_6\text{H}_5\text{N}$  at 90° gives the triacetate (IV), m.p. 114—115°. (I) is hydrolysed by  $\text{K}_2\text{CO}_3$ - $\text{KHCO}_3$  in aq. MeOH at room temp. into 21-diazopregnane-3( $\alpha$ ):12( $\beta$ )-diol-20-one 12-monoacetate, which in anhyd. AcOH at 105° passes into pregnane-3( $\alpha$ ):12( $\beta$ ):21-triol-20-one 12:21-diacetate (V), two forms, m.p.  $\sim 72$ —95° and 156—158°,  $[\alpha]_D^{19} +150.7^\circ \pm 2^\circ$  in  $\text{COMe}_2$ , with some (III). (V) is acetylated to (IV). Excess of  $\text{CrO}_3$  oxidises (III) to pregnane-21-ol-3:12:20-trione acetate (VI), m.p. 189—191°,  $[\alpha]_D^{17} +153.0^\circ \pm 3^\circ$  in  $\text{COMe}_2$ , whereas 1 equiv. of  $\text{CrO}_3$  affords a mixture from which (?) pregnane-3( $\alpha$ ):21-diol-12:20-dione 21-monoacetate, m.p. 149—151°,  $[\alpha]_D^{19} +157.6^\circ \pm 3^\circ$  in  $\text{COMe}_2$ , is isolated; it is further oxidised to (VI). In boiling  $\text{C}_6\text{H}_6$ - $\text{COMe}_2$ , (III) and  $\text{Al}(\text{OPh})_3$  yield pregnane-12( $\beta$ ):21-diol-3:20-dione 21-monoacetate (VII), m.p. 190—192°,  $[\alpha]_D^{14} +146.3^\circ \pm 3^\circ$  in  $\text{COMe}_2$ ; this is oxidised by  $\text{CrO}_3$  in AcOH at room temp. to (VI). (V) is oxidised by  $\text{CrO}_3$  to pregnane-12( $\beta$ ):21-diol-3:20-dione diacetate (VIII), m.p. 120—122°,  $[\alpha]_D^{17} +142.4^\circ \pm 4^\circ$  in  $\text{CHCl}_3$ , also obtained from (VII) and  $\text{Ac}_2\text{O}$  in  $\text{C}_6\text{H}_5\text{N}$  at 20° and then 90°. Bromination followed by treatment with boiling  $\text{C}_6\text{H}_5\text{N}$  converts (VI), (VII), and (VIII) into  $\Delta^4$ -pregnen-21-ol-3:12:20-trione acetate, m.p. 182—184°,  $[\alpha]_D^{14} +228.6^\circ \pm 3^\circ$  in  $\text{COMe}_2$ ,  $\Delta^4$ -pregnene-12( $\beta$ ):21-diol-3:20-dione 21-monoacetate (IX), m.p. 182—184°,  $[\alpha]_D^{21} +203.7^\circ \pm 2^\circ$ ,  $[\alpha]_{5461}^{21} +251.6^\circ \pm 2^\circ$  in  $\text{COMe}_2$ , and  $\Delta^4$ -pregnene-12( $\beta$ ):21-diol-3:20-dione diacetate (X), m.p. 158—159°,  $[\alpha]_D^{17} +197.7^\circ \pm 5^\circ$  in  $\text{COMe}_2$ , respectively. These show the ultra-violet absorption spectrum characteristic of  $\alpha\beta$ -unsaturated ketones. Acidic or cautious alkaline hydrolysis converts them respectively into  $\Delta^4$ -pregnen-21-ol-3:12:20-trione, m.p. 180—183°,  $[\alpha]_D^{23} +238.9^\circ \pm 3^\circ$ ,  $[\alpha]_{5461}^{23} +298^\circ \pm 3^\circ$  in dioxan,  $[\alpha]_D^{23} +215.1^\circ \pm 2^\circ$ ,  $[\alpha]_{5461}^{23} +265.8^\circ \pm 2^\circ$  in  $\text{COMe}_2$ ,  $\Delta^4$ -pregnene-12( $\beta$ ):21-diol-3:20-dione, m.p. 98—124° (decomp.),  $[\alpha]_D^{21} +186.1^\circ \pm 2^\circ$ ,  $[\alpha]_{5461}^{21} +221.1^\circ \pm 2^\circ$  in dioxan, and its 12-monoacetate, m.p. 188—192°,  $[\alpha]_D^{19} +185.3^\circ \pm 2^\circ$ ,  $[\alpha]_{5461}^{19} +226.3^\circ \pm 3^\circ$  in  $\text{COMe}_2$ . Preliminary experiments appear to show that (IX) and (X) are at any rate less potent than corticosterone in the Everse-de Fremery test and that (X) is inactive in 4-mg. doses in the anti-insulin test. M.p. are corr. (block); limit of error  $\pm 2^\circ$ .

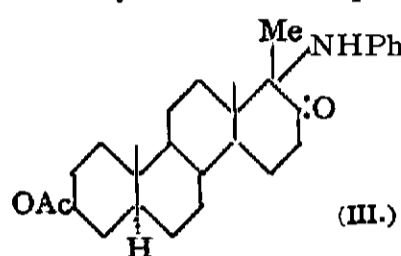
H. W.

**Steroids and sex hormones. LXXXIII. 4-Homocholestanone and A-homodihydrotestosterone.** M. W. Goldberg and H. Kirchensteiner (*Helv. Chim. Acta*, 1943, 26, 288—301).—The methods used for the enlargement of ring D have been extended to that of ring A. Catalytic reduction ( $\text{PtO}_2$  in AcOH at room temp.) of cyclohexanone cyanohydrin gives 1-aminomethylcyclohexanol (I) (hydrochloride, m.p. 210—212°; N-Bz derivative, m.p. 142—143°) and di-1-hydroxyhexahydrobenzylamine (hydrochloride, m.p. 250—252°; N-NO-compound, m.p. 133—134°); the yield of (I) is greatly increased if  $\text{HCl}$  is added to the reaction mixture. Similar hydrogenation of cyclohexanone cyanohydrin acetate leads to dihexahydrobenzylamine, isolated as the NO-derivative, m.p. 100—101°. Cholestanone cyanohydrin is hydrogenated ( $\text{PtO}_2$  in AcOH at room temp.) to 3-hydroxy-3-aminomethylcholestanone, m.p. 194—197° [hydrochloride; N-Ac (II), m.p. 227—228°, and  $\text{Ac}_2$ , m.p. 176—178°, derivatives], transformed by  $\text{HNO}_2$  into A-homocholestanone, m.p. 85—87°,  $[\alpha]_D +50^\circ$  in  $\text{CHCl}_3$  (semicarbazone, m.p. 239—242°; oxime, m.p. 197—199°). Hydrogenation of cholestanone cyanohydrin acetate, m.p. 123—126°, yields (II), Ac wandering from O to N. 17-Acetoxydihydrotestosterone gives a very unstable cyanohydrin, m.p. 175—187° (characterised as the 3:17-diacetate, m.p. 198—200°), hydrogenated to 17-acetoxy-3-aminomethylandrostan-3-ol hydrochloride, m.p. 295—297° (decomp.) [17-acetoxy-3-acetamidomethylandrostan-3-ol has m.p. 224—226°], converted by  $\text{HNO}_2$  and subsequent hydrolysis (N-MeOH-KOH) into A-homodihydrotestosterone (III), m.p. 197—199°,  $[\alpha]_D +108.5^\circ$  in  $\text{CHCl}_3$  [oxime, m.p. 225—227°; acetate, m.p. 146—148° (semicarbazone, m.p. 239—241°)]; (III) is devoid of pharmacological activity. Cholestanone is converted by  $\text{NaOEt}$  and isoamyl formate in  $\text{Et}_2\text{O}$  at room temp. into the  $\text{OH}\cdot\text{CH}$  compound, m.p. 176—178°, and by  $\text{PhCHO}$  in EtOH containing a little aq. NaOH into two  $\text{CHPh}$  derivatives, m.p. 145—146° and 126—128°, and a  $\text{OH}\cdot\text{CHPh}$  compound, m.p. 184—186°. Benzylidene- and bromo-, m.p. 113—115°, -A-homocholestanone are described. Androstenedione dicyanohydrin diacetate has m.p. 171—172°. M.p. are corr.

H. W.

**Constituents of the adrenal cortex and related compounds. LVII. 17-Hydroxy-20-ketosteroids and the mechanism of their rearrangement into polyhydrochrysene derivatives.** C. W. Shoppee and D. A.

Prins (*Helv. Chim. Acta*, 1943, **26**, 185—200).—It is deduced from theoretical considerations that the hydration of acetylenylandrostan derivatives is most likely to occur without ring enlargement if OH at C<sub>(17)</sub> is etherified or esterified, if an amine instead of H<sub>2</sub>O is added at the triple linking and if the experiment is performed in neutral solution. Thus 3(β):17(a)-diacetoxy-17-acetylenylandrostan is converted by aq. HgCl<sub>2</sub> and NH<sub>2</sub>Ph in C<sub>6</sub>H<sub>6</sub> at 60—62° (cf. Stavely, A., 1940, II, 180; 1942, II, 147) into 3(β):17(a)-diacetoxyallopregnan-20-one (I), m.p. 227—229°, [α]<sub>D</sub><sup>20</sup> +2.5°±2° in COMe<sub>2</sub> (cf. Ruzicka *et al.*, A., 1939, II, 327), converted by boiling 4% KOH-MeOH into 3(β):17(a)-dihydroxy-17a-methyl-D-homoandrostan-17-one (II), m.p. 295—300° (3-acetate, m.p. 243—244°). (I) is converted by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O-NaOEt-EtOH at 180° into 3(β)-hydroxy-17a-methyl-Δ<sup>17</sup>-D-homoandrosten-17-one, m.p. 159—160°, also obtained similarly from (II); this is hydrogenated (PtO<sub>2</sub> in AcOH) and then oxidised to 17a-methyl-D-homoandrostan-3-one, m.p. 180—182° (Ruzicka *et al.*, A., 1940, II, 180, 218), which is converted by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O and NaOEt-EtOH at 175° into 17a-methyl-D-homoandrostan-3-one. (I) is not hydrogenated in presence of PtO<sub>2</sub> in AcOH at 20° or 100° or in presence of Raney Ni in MeOH at 100° or 120°. 17(a)-Hydroxy-3(β)-acetoxy-17-acetylenylandrostan is transformed similarly into a small proportion of a substance, m.p. 176—177°, which has not been investigated further, the compound (III), m.p. 232—233°, [α]<sub>D</sub><sup>23</sup> -103.3°±6° in dioxan [NO-derivative, m.p. 194° (decomp.)] (obtained by rearrangement of the anil), and 17(a)-hydroxy-3(β)-acetoxyallopregnan-20-one (IV), apparently two forms, m.p. 184—186° and 190—192°, [α]<sub>D</sub><sup>23</sup> -24.3°±3°, [α]<sub>D</sub><sup>23</sup> -29.4°±3° in dioxan. (IV) is oxidised (CrO<sub>3</sub> in AcOH at room temp.) and then hydrolysed (K<sub>2</sub>CO<sub>3</sub>-aq. MeOH) to t-androsterone and 17a(β)-hydroxy-3(β)-acetoxy-17a-methylandrostan-17-one, m.p. 158—159°. (IV) is hydrogenated (PtO<sub>2</sub> in EtOH) and then acetylated (Ac<sub>2</sub>O-C<sub>6</sub>H<sub>5</sub>N at room temp.) to 17(a)-hydroxy-3(β):20(β)-diacetoxyallopregnane, flat platelets which are transformed at ~185° into rectangular prisms, m.p. 200—202°; this appears to be the sole product. (IV), Ac<sub>2</sub>O, and C<sub>6</sub>H<sub>5</sub>N at 100° yield 3(β):17(a)-diacetoxyallopregnan-20-one, m.p. 227—229°. M.p. are corr. (block); limit of error ±2°.



is oxidised (CrO<sub>3</sub> in AcOH at room temp.) and then hydrolysed (K<sub>2</sub>CO<sub>3</sub>-aq. MeOH) to t-androsterone and 17a(β)-hydroxy-3(β)-acetoxy-17a-methylandrostan-17-one, m.p. 158—159°. (IV) is hydrogenated (PtO<sub>2</sub> in EtOH) and then acetylated (Ac<sub>2</sub>O-C<sub>6</sub>H<sub>5</sub>N at room temp.) to 17(a)-hydroxy-3(β):20(β)-diacetoxyallopregnane, flat platelets which are transformed at ~185° into rectangular prisms, m.p. 200—202°; this appears to be the sole product. (IV), Ac<sub>2</sub>O, and C<sub>6</sub>H<sub>5</sub>N at 100° yield 3(β):17(a)-diacetoxyallopregnan-20-one, m.p. 227—229°. M.p. are corr. (block); limit of error ±2°.

H. W.

**Constituents of the adrenal cortex and related compounds. LVIII. Rearrangement of 17-hydroxy-20-ketosteroids into polyhydrochrysene derivatives. Acetylations in the presence of boron fluoride.** C. W. Shoppee and D. A. Prins (*Helv. Chim. Acta*, 1943, **26**, 201—223).—Hydration of 3(β):17(a)-dihydroxy-17-acetylenyl-Δ<sup>5</sup>-androsten-17-one by the method of Stavely (A., 1940, II, 180; 1942, II, 147) affords 3(β):17(a)-dihydroxy-Δ<sup>5</sup>-pregnen-20-one (I), m.p. 176—179°, [α]<sub>D</sub><sup>21</sup> -60°±3° in CHCl<sub>3</sub> (acetate, m.p. 187—188°, [α]<sub>D</sub><sup>18</sup> -61.3°±5° in CHCl<sub>3</sub>), and 17a-anilino-3(β)-hydroxy-17a-methyl-Δ<sup>5</sup>-D-homoandrosten-17-one, m.p. 150°, [α]<sub>D</sub><sup>18</sup> -186.6°±7° in CHCl<sub>3</sub> [acetate, m.p. 236—238°; NO-derivative, m.p. 140° and 170—174° (decomp.) after resolidification], identical with the "anil" of Stavely (*loc. cit.*) and Goldberg *et al.* (A., 1939, II, 553). (I) is converted by Ac<sub>2</sub>O and C<sub>6</sub>H<sub>5</sub>N at 120° into the diacetate (II), m.p. 193—195°, [α]<sub>D</sub><sup>23</sup> -55.9°±2° in dioxan, with a compound, m.p. 177—178°, [α]<sub>D</sub><sup>18</sup> -79°±2° in CHCl<sub>3</sub>, which may be identical with it. Hydration (Stavely) of 3(β):17(a)-diacetoxy-20-acetylenyl-Δ<sup>5</sup>-androsten-17-one yields (II), also obtained by the BF<sub>3</sub> method. Filtration of (I) in dry C<sub>6</sub>H<sub>6</sub> through Al<sub>2</sub>O<sub>3</sub> followed by immediate elution causes partial conversion into 3(β):17a(β)-dihydroxy-17a-methyl-Δ<sup>5</sup>-D-homoandrosten-17-one (III), m.p. 176—178°, [α]<sub>D</sub><sup>18</sup> -105.6°±3° in CHCl<sub>3</sub>; if undried solvents are used and longer contact with the column is permitted the change becomes more complete. 17a(β)-Hydroxy-3(β)-acetoxy-17a-methyl-Δ<sup>5</sup>-D-homoandrosten-17-one, m.p. 176° (change at 160°), [α]<sub>D</sub><sup>17</sup> -91.1°±4° in CHCl<sub>3</sub>, is obtained similarly or by acetylation of (III). (III) is converted by Al(OBu)<sub>3</sub> in abs. C<sub>6</sub>H<sub>6</sub>-COMe<sub>2</sub> at 100° into 17a(β)-hydroxy-17a-methyl-Δ<sup>4</sup>-D-homoandrosten-3:17-dione, m.p. 178—180°, [α]<sub>D</sub><sup>17</sup> +60.8°±3° in CHCl<sub>3</sub>. (II) is hydrolysed by boiling KOH-MeOH to 3(β):17a(a)-dihydroxy-17a-methyl-Δ<sup>5</sup>-D-homoandrosten-17-one, prisms which pass into hexagonal prisms at ~260° and at 290° into rodlets which melt at 302—305° (acetate, m.p. 277—278°, [α]<sub>D</sub><sup>19</sup> -100.9°±4° in dioxan). (I) is hydrogenated (PtO<sub>2</sub> in AcOH) and then acetylated to 17(a)-hydroxy-3(β):20(β)-diacetoxyallopregnane, m.p. 202—204°, [α]<sub>D</sub><sup>21</sup> -7.9°±3° in CHCl<sub>3</sub>. Nieuwland's mixture (BF<sub>3</sub>, Ac<sub>2</sub>O, AcOH, and HgO) (cf. A., 1930, 745) causes hydration of the triple linking through an unknown series of intermediates whereby the presence of Hg<sup>2+</sup> is essential, and causes acetylation of free OH. The prep. of the following compounds proves it to be a very powerful acetylating agent: 3(β):17a(β)-diacetoxy-17a-methyl-Δ<sup>5</sup>-D-homoandrosten-17-one, m.p. 238—240°, [α]<sub>D</sub><sup>22</sup> -68.4°±3° in dioxan, from (I) or (III) [reduced (H<sub>2</sub>, PtO<sub>2</sub>, AcOH) to 3(β):17a(β)-diacetoxy-17a-methyl-D-homoandrostan-17-one (IV), m.p. 221—222°, [α]<sub>D</sub><sup>18</sup> -6.1°±3° in COMe<sub>2</sub>]; (IV), from its 3-monoacetate, m.p. 159—160°, [α]<sub>D</sub><sup>15</sup> -34.8°±4° in dioxan, obtained by rearrangement (Al<sub>2</sub>O<sub>3</sub>) of 17(a)-hydroxy-3(β)-acetoxyallopregnan-20-one (V); (IV) from (V); 3(β):17a(a)-diacetoxy-17a-methyl-Δ<sup>5</sup>-D-homoandrosten-17-one, m.p. ~248° after changing at ~240, [α]<sub>D</sub><sup>19</sup> -32.8°±4° in CHCl<sub>3</sub>, reduced to the

-D-homoandrostan-7-one, m.p. 232—235° (change at 228°), [α]<sub>D</sub><sup>16</sup> 0°±4° in COMe<sub>2</sub>. M.p. are corr. (block); limit of error ±2°.

H. W.

ψ-Sapogenin compounds.—See B., 1943, III, 135.

## V.—TERPENES AND TRITERPENOID SAPOGENINS.

**Inversion of menthone with trichloroacetic acid in aprotic solvents.**

A. Weissberger (*J. Amer. Chem. Soc.*, 1943, **65**, 102—110).—The equilibrium, *l*-(I) ⇌ *d*-iso-menthone, in presence of CCl<sub>3</sub>·CO<sub>2</sub>H (II) in C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>14</sub>, and CHCl<sub>3</sub> at 20° is investigated polarimetrically and cryoscopically. The catalytic activity per mol. of acid is a max. when the molar ratio (I):(II) = 1:2 for the range (I) = 0.1—1.0 mol. per l. At const. [(II)], the reaction rate falls with increasing [(I)], the effect being greater if the (II) is in excess. The temp. coeff. from 20° to 50° gives a heat of activation = 6200 g.-cal. [α] of the equilibrium mixture depends on the [(II)], since (i) (II) affects the [α] and (ii) higher [(II)] decreases the proportion of (I). Inversion occurs by interaction of a (I)-(II) complex with another mol. of (II) or by rearrangement of a complex, I(I)-2(II). Tubandt's view (A., 1911, ii, 28) of the nature of "Rechtsmenthon" is confirmed.

R. S. C.

**Effect of solvents in chemical reactions. III. Influence of addenda on the inversion of *l*-menthone with acids in benzene.** A. Weissberger (*J. Amer. Chem. Soc.*, 1943, **65**, 242—245; cf. A., 1932, 22).—PhOH, PhOMe, COPh<sub>2</sub>, *l*-menthol, COPhMe, COMe<sub>2</sub>, *l*-menthone, and Et<sub>2</sub>O reduce the rate of inversion of *l*-menthone (I) by CCl<sub>3</sub>·CO<sub>2</sub>H in C<sub>6</sub>H<sub>6</sub> at 20±0.1°. The quant. results, given as % acid eliminated (order of efficiency as above), parallel those for salt-formation of *p*-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Ph and interaction of CHN<sub>2</sub>·CO<sub>2</sub>Et with CCl<sub>3</sub>·CO<sub>2</sub>H (A., 1931, 1375). Inversion of (I) by HCl in C<sub>6</sub>H<sub>6</sub> is retarded by Et<sub>2</sub>O but accelerated by PhOH.

R. S. C.

**Inversion of *l*-menthone and reaction of diazoacetic ester with chloroacetic acids.** A. Weissberger (*J. Amer. Chem. Soc.*, 1943, **65**, 245—246).—Decomp. of CHN<sub>2</sub>·CO<sub>2</sub>Et and inversion of *l*-menthone by CCl<sub>3</sub>·CO<sub>2</sub>H, CHCl<sub>2</sub>·CO<sub>2</sub>H, or CH<sub>2</sub>Cl·CO<sub>2</sub>H in C<sub>6</sub>H<sub>6</sub> all agree with the Brönsted relation.

R. S. C.

**Isomeric Δ<sup>1</sup>-menthenes (carvomenthenes).** A. A. Dodge and E. Kremers (*J. Amer. Pharm. Assoc.*, 1942, **31**, 525—527).—*l*- and *d*-Carvoxime are reduced (H<sub>2</sub>; Raney Ni) to *d*-(I), b.p. 77—78°/7 mm., [α]<sub>D</sub><sup>23</sup> +5.92° [hydrochloride, m.p. 192—195°; *picrate*, m.p. 184—185° (decomp.)] (cf. Read and Johnston, A., 1934, 413), and *l*-carvomenthylamine (II), b.p. 81.5—82.0°/9 mm., [α]<sub>D</sub><sup>23</sup> -8.34° [hydrochloride, m.p. 197—198°; *picrate*, m.p. 184—185° (decomp.)], respectively. (I), treated with HNO<sub>2</sub>, refluxed, steam-distilled, and fractionated in vac., affords two fractions, (a), b.p. 43.8—45.5°/0.02—0.03 mm., [α]<sub>D</sub><sup>25</sup> -1.22° (3:5-dinitrobenzoate, m.p. 105—106°), and (b), b.p. 44.0—45.5°/0.02 mm., [α]<sub>D</sub><sup>25</sup> +1.62°; similarly, (II) gives (a), b.p. 40.5—42.5°/0.025 mm., [α]<sub>D</sub><sup>20</sup> +0.88° (3:5-dinitrobenzoate, m.p. 108.5—109.5°), and (b), b.p. 42.5—44.5°/0.025 mm., [α]<sub>D</sub><sup>20</sup> -2.18°. These carvomenthols preps. readily lose H<sub>2</sub>O during fractionation, giving a menthene fraction, the carvomenthol from (I) giving a product of [α]<sub>D</sub><sup>20</sup> +19.54° [nitroschloride (impure), m.p. 81.5—83°, and its nitrolbenzylamine base, m.p. 107—107.5°], and that from (II) a product of [α]<sub>D</sub><sup>20</sup> -10.98° (nitroschloride, m.p. 98—99°). When dehydrated by refluxing with anhyd. CuSO<sub>4</sub> at 180—200° for 9 hr., the carvomenthol from (I) yields a carvomenthene fraction, [α]<sub>D</sub><sup>23</sup> +11.44° (nitroschloride, m.p. 90—91°, and its nitrolbenzylamine, m.p. 106—107°, and nitrolmorpholine base, m.p. 159—160°), and that from (II) a carvomenthene fraction, [α]<sub>D</sub><sup>25</sup> -8.65° (nitroschloride, m.p. 90—91°, and its nitrolbenzylamine, m.p. 107—107.5°, and nitrolmorpholine base, m.p. 159—160°) (cf. Johnston and Read, A., 1935, 1245). Vals. of *d* and *n* are also given.

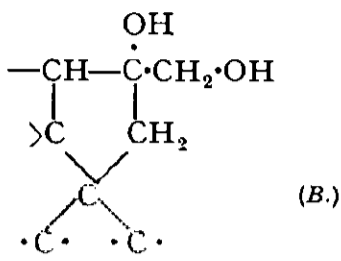
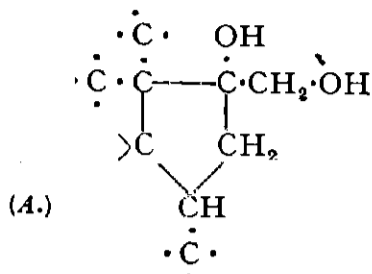
F. O. H.

**Lavandulol, a new monoterpene alcohol from oil of lavender.**—See A., 1943, II, 181.

**Volatile vegetable compounds. XXII. Composition of "natural" cedrene and constitution of "synthetic" cedrene.** Y. R. Naves, G. Papazian, and E. Perrottet (*Helv. Chim. Acta*, 1943, **26**, 302—337).—"Synthetic" cedrene (termed *α*-cedrene) (I), b.p. 100°/3.5 mm., [α]<sub>D</sub><sup>20</sup> -91.22° to -91.33°, obtained by dehydration of cedrol, m.p. 86—86.5°, [α]<sub>D</sub><sup>18</sup> +13.06° in abs. EtOH, +8.76° in CH<sub>2</sub>Ph·OH, +14.26° in dioxan, is a well-defined sesquiterpene with an endocyclic ethylenic linking. It is possibly a 2:8-dimethyl-2:5-endoisopropylidene-[0:3:5]-dicyclo-Δ<sup>8</sup>-decene (2:8-dimethyl-2:5-endoisopropylidene-1:2:3:4:5:6:7:10-octahydroazulene). "Natural" cedrene, obtained by fractional distillation from American oil of red cedar, is a mixture containing a considerable proportion of (I), its isomeride with an exocyclic CH<sub>2</sub> (β-cedrene), and a mixture of tricyclic sesquiterpenes which appear to be allied closely in structure to the cedrenes. (I) with H<sub>2</sub>O<sub>2</sub> in presence of H<sub>2</sub>SO<sub>4</sub> and AcOH gives an excellent yield of cedranone, b.p. 134°/4 mm., *α*<sub>D</sub> -84.70° (*oxime*, m.p. 103.5—104°, [α]<sub>D</sub> -78.59° in CHCl<sub>3</sub>, -69.14° in MeOH). The material, sol. in acid, obtained by Treibs (A., 1935, 983) by the action of conc. H<sub>2</sub>SO<sub>4</sub> on the cedrenes is a dehydrosesquiterpene or mixture of dehydrosesquiterpenes.

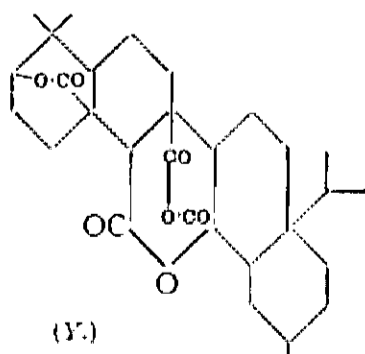
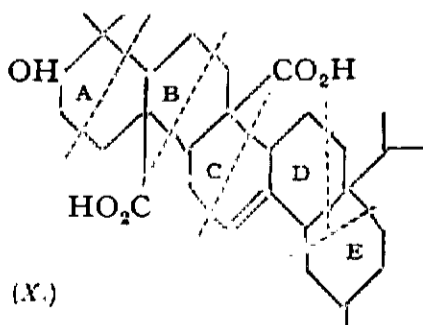
H. W.

**Constitution of cafesterol. III. Constitution of cafestol.** A. Wettstein and K. Miescher (*Helv. Chim. Acta*, 1943, 26, 631—641; cf. A., 1942, II, 371).—Since cafesterol has been shown not to belong to the sterol group its name is modified to "cafestol" (I). The union of the cyclopentane ring in (I) is probably in accordance with (A) or (B). Floridin has proved very useful in the chromatographic purification of cafestyl acetate (II), m.p. 173—175°,  $[\alpha]_D^{20} -91^\circ \pm 2^\circ$  in  $\text{CHCl}_3$ ; it gives slowly and weakly a pure blue colour

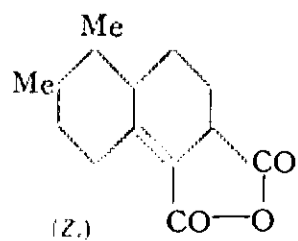


with mineral acids but the intense blue fluorescence under the Hg-vapour lamp is no longer observed. The residues from (II) yield a (non-homogeneous) kahweyl acetate, m.p.  $\sim 146^\circ$ ,  $[\alpha]_D^{24} -234^\circ$  in  $\text{CHCl}_3$ , characterised by high extinction, intense green-blue colour with mineral acids, reaction with  $(\text{CH}\cdot\text{CO})_2\text{O}$ , and non-fluorescence in ultra-violet light; it is possibly identical with the compound of Bengis *et al.* (A., 1932, 975). Alkaline hydrolysis of the  $\text{Me}_2$  ester (A., 1942, II, 198) from epoxycafestanediol gives a *Me H* ester,  $\text{C}_{20}\text{H}_{30}\text{O}_5$ , m.p. 150.5—152°, and ultimately a non-cryst. product; hydrolysis resembles that of  $\text{Me}_2$  3*t*-acetoxy- $\Delta^5$ -ætiobilienate. Probably, therefore,  $\text{C}_{(5)}$  or  $\text{C}_{(3)}$  closely resembles  $\text{C}_{(13)}$  of the steroid skeleton and is quaternary or at any rate *tert*. Differences, however, are found between the cyclopentane ring of (I) and ring D of the steroid mol. The colour reactions of  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$  with (I) and its derivatives are less intense and develop much more slowly than those of 17-ketosteroids. Further, epoxynorcafestanone A and epoxynorcafestadienone do not condense with  $\text{ArCHO}$  (see A., 1943, II, 199). M.p. are corr. H. W.

**Triterpenes. LXXIII. Pyrolysis of a product of the transformation of quinovic acid.** L. Ruzicka and G. Anner (*Helv. Chim. Acta*, 1943, 26, 129—142).—The dilactonic dicarboxylic anhydride (I), m.p. 260° (decomp.) (cf. Schmitt *et al.*, A., 1940, II, 88), obtained by the oxidation of novaquinone with  $\text{H}_2\text{O}_2$  (improved prep.) is pyrolysed at ordinary pressure. The acidic products of pyrolysis consist of a solid and a liquid portion, the former of which is separated by fractional crystallisation into two isomeric dicarboxylic acids,  $\text{C}_{14}\text{H}_{20}\text{O}_4$ , m.p. 183—184°,  $[\alpha]_D -155^\circ$  in EtOH (II) [ $\text{Me}_2$  ester, a liquid which gives a distinct yellow colour with  $\text{C}(\text{NO}_2)_4$ ], and m.p. 200—202°,  $[\alpha]_D -170^\circ$  in EtOH, either of which is transformed by boiling  $\text{Ac}_2\text{O}$  into the anhydride (III),  $\text{C}_{14}\text{H}_{18}\text{O}_3$ , m.p. 80—80.5°, which passes into (II) when hydrolysed by 0.1*N*-KOH. Dehydrogenation of (III) under varied conditions in presence of Pd-C or Se gives 1:2- $\text{C}_{10}\text{H}_8\text{Me}_2$  [identified by the m.p. and mixed m.p. of its picrate, styphnate, and additive compound with  $\text{C}_6\text{H}_3(\text{NO}_2)_3$ ] and 1:2-dimethylnaphthalene-5:6-dicarboxylic anhydride (IV), m.p. 164.5—165.5°. The established formation of 1:8-dimethyl- and 1:2:8-trimethyl-picene (V) by the dehydrogenation of quinovic acid (VI) and of pure (V) by the similar treatment of norquinovenol proves that 1:2- $\text{C}_{10}\text{H}_8\text{Me}_2$  and (IV) can arise only from rings A and B of the pentacyclic skeleton of (VI). A modification of Schmitt's formula (*loc. cit.*) for (VI) is therefore necessary whereby it is also brought into conformity with the isoprene rule. (VI), (I), and (III) have accordingly the respective formulæ X, Y, and Z, whereby the structure assigned to rings D and E is provisional. Treatment of the neutral portion of the pyrolysis products



with Girard's reagent T gives two portions which in composition, (?)  $\text{C}_{14}\text{H}_{22}\text{O}$ ,  $[\alpha]_D$ , and  $n_D^{19}$  are very closely similar but are distinguished from one another in ultra-violet absorption spectrum.



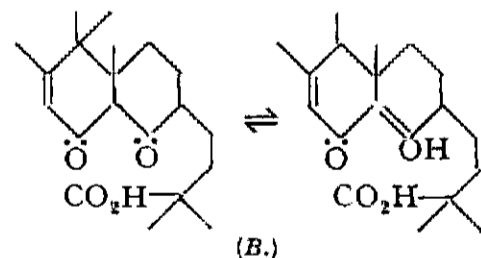
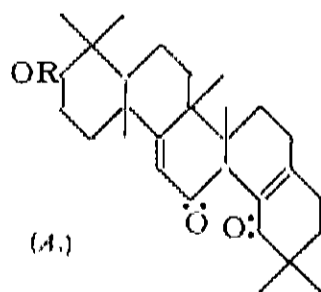
The reacting portion thus appears to be a mixture of ketones a fraction of which is  $\alpha\beta$ -unsaturated. This portion gives in small yield a 2:4-dinitrophenylhydrazones, m.p. (indef.) 125—130°, corresponding in composition to  $\text{C}_{14}\text{H}_{22}\text{O}$ . This fraction is treated with  $\text{MgMeI}$ , dehydrated by  $\text{KHSO}_4$  at 185—190°, and then dehydrogenated with Pd-C or Se at 340—420°, whereby a liquid  $\text{C}_{13}\text{H}_{18}\pm\text{CH}_2$  is ultimately obtained which does not combine with picric acid or  $\text{C}_6\text{H}_3(\text{NO}_2)_3$  and in

which the presence of a  $\text{C}_6\text{H}_6$  ring is established spectroscopically. This may possibly be explained by the assumption that ring E is five-membered. M.p. are corr. H. W.

**Triterpenes. LXXIV. Dehydrogenation of quinovic acid to chrysene hydrocarbons.** L. Ruzicka, A. Grob, and G. Anner [with V. Prelog and K. Huber] (*Helv. Chim. Acta*, 1943, 26, 254—264; cf. Wieland *et al.*, A., 1936, 849).—Quinovic acid (I) is dehydrogenated by Se at 360° and the product is extracted successively with light petroleum, b.p. 40—70°, and  $\text{C}_6\text{H}_6$ ; from the last solvent 1:8-dimethylpicene (II) is isolated. The portion sparingly sol. in light petroleum after being purified chromatographically gives a hydrocarbon,  $\text{C}_n\text{H}_m$ , m.p. 193—195°, softens slightly at 190° (additive compound with 2:7-dinitroanthraquinone,  $\text{C}_{24}\text{H}_{24}\cdot\text{C}_{14}\text{H}_8\text{O}_6\text{N}_2$ , m.p. 220—230°). The same hydrocarbons are obtained by the dehydrogenation of pyroquinovatrienic acid (Wieland *et al.*, A., 1939, II, 425). (I) is converted by Se at 330—340° into (II) anhydropyroquinovic acid, and two hydrocarbons,  $\text{C}_n\text{H}_m$ , m.p. 239—240° (additive compound with 2:7-dinitroanthraquinone) and 233.5—234.5° respectively. Spectroscopically they very closely resemble alkylchrysenes, thus indicating that ring E of (I) is five-membered.

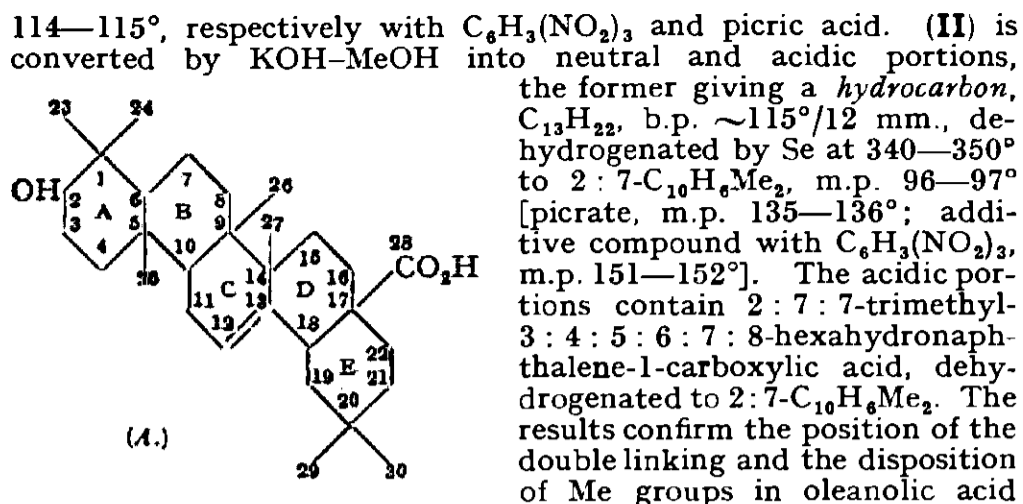
The action of the Mg compound from  $\beta$ -o-tolylethyl bromide on 1-keto-5:6-dimethyl-1:2:3:4-tetrahydronaphthalene followed by elimination of  $\text{H}_2\text{O}$  from the product affords  $\alpha$ -o-tolyl- $\beta$ -5:6-dimethyl-1:2:3:4-tetrahydronaphthylethane, m.p. 53—54°, dehydrogenated by Pd-C at 320° to  $\alpha$ -o-tolyl- $\beta$ -5:6-dimethylnaphthylethane, m.p. 60°, which is converted by  $\text{AlCl}_3$  in  $\text{CS}_2$  into 1:7:8-trimethylchrysene, m.p. 281—282°. Similarly,  $\alpha$ -2:3-dimethylphenyl- $\beta$ -5:6-dimethyl-1:2:3:4-tetrahydronaphthylethane, b.p. 165°/1 mm., is transformed successively into  $\alpha$ -2:3-dimethylphenyl- $\beta$ -5:6-dimethylnaphthylethane, m.p. 90.5—91.5°, and 1:2:7:8-tetramethylchrysene, m.p. 298—299°. M.p. are corr. H. W.

**Triterpenes. LXXV. Position of the carboxyl group in oleanolic and glycyrrhetic acid.** L. Ruzicka, O. Jeger, and M. Winter (*Helv. Chim. Acta*, 1942, 26, 265—279).—Oxidation of Me acetyloleanolate (I) by  $\text{SeO}_2$  in dioxan at 200° gives Me diketoacetyldehydro-oleanolate (II), m.p. 251—252° (cf. A., 1939, II, 331), converted by mild alkaline hydrolysis into Me diketodehydro-oleanolate, m.p. 263—265° (high vac.), which does not give a yellow colour with  $\text{C}(\text{NO}_2)_4$  and is reconverted by  $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$  into (II) and the corresponding acid, which passes in boiling xylene into nor- $\beta$ -amyradienedionol acetate (III) (A; R = Ac), m.p. 323—324° (high vac.),  $[\alpha]_D +227^\circ$ . Energetic hydrolysis of (II) leads to nor- $\beta$ -amyradienedionol (A; R = H) (IV), m.p. 295° (high vac.),  $[\alpha]_D +233^\circ$ , acetylated to (III), which is also obtained directly from (I). (III) is transformed by  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in EtOH at 200° into the pyridazine derivative,  $\text{C}_{29}\text{H}_{42}\text{ON}_2$ , m.p. 304—306° (vac.),  $[\alpha]_D +275^\circ$ , and is hydrogenated ( $\text{PtO}_2$  in AcOH at 90°) to the substances,  $\text{C}_{31}\text{H}_{48}\text{O}_3$ , m.p. 218—219°, and  $\text{C}_{31}\text{H}_{46}\text{O}_4$ , m.p. 271—273°,  $[\alpha]_D +139.4^\circ$ . (II) is oxidised by  $\text{CrO}_3$  in AcOH at 80° to Me acetyldiketodehydro-oleanolate oxide, m.p. 243—245°,  $[\alpha]_D -148^\circ$ , which does not give a positive reaction with  $\text{C}(\text{NO}_2)_4$  and is converted by  $\text{KOH}-\text{MeOH}$  at 200° into the nor-acid (B), m.p. 249—251°,  $[\alpha]_D +63^\circ$  in  $\text{C}_5\text{H}_5\text{N}$  (Me ester, m.p.



203—204°), which gives a yellow colour with  $\text{C}(\text{NO}_2)_4$ , and (IV). Ketoacetyloleanolic acid (V) is transformed by Br in AcOH into ketoacetyldehydro-oleanolic acid, m.p. 288—289°,  $[\alpha]_D +233^\circ$ , which can be sublimed unchanged at 260—270°/high vac. and gives a pale yellow colour with  $\text{C}(\text{NO}_2)_4$ . (V) is decarboxylated in quinoline (cf. A., 1939, II, 29) to acetylnor- $\beta$ -amyradienolone, m.p. 237—238° (high vac.),  $[\alpha]_D +52^\circ$ , and acetylnor- $\beta$ -amyradienolone, m.p. 202°,  $[\alpha]_D +150^\circ$ . The acetylnor- $\beta$ -amyradienolone obtained by the oxidation of glycyrrhetic acid is oxidised by  $\text{CrO}_3$  in AcOH to bisnor- $\beta$ -amyradienolone acetate, m.p. 246—248° [semicarbazone, m.p. 222—224° (decomp.)]. These observations are not compatible with the constitution assigned to oleanolic and other triterpenic acids by Bilham *et al.* (A., 1942, II, 148) but are consistent with Haworth's variant of the formulation of the  $\beta$ -amyrin-oleanolic acid group. M.p. are corr. and  $[\alpha]_D$  are in  $\text{CHCl}_3$  unless otherwise stated. H. W.

**Triterpenes. LXXVI. Pyrolysis of methyl hydrogen isooleanone-lactonedicarboxylate.** L. Ruzicka, F. C. van der Sluys-Veer, and O. Jeger (*Helv. Chim. Acta*, 1943, 26, 280—288; cf. A., 1939, II, 220).—Pyrolysis of Me H isooleanone-lactonedicarboxylate gives a product separated by Girard's reagent T into a ketonic (I) and a non-ketonic (II) portion. The semicarbazone, m.p. 203—204°, from (I) is converted by  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  and  $\text{NaOEt}-\text{EtOH}$  at 200° into a hydrocarbon, b.p.  $\sim 120^\circ$ /12 mm., dehydrogenated by Se at 340—350° to 1:6- $\text{C}_{10}\text{H}_8\text{Me}_2$ , identified by its compounds, m.p. 132—133° and



(A) but are not reconcilable with the formula of Bilham *et al.* (A., 1942, II, 148). A suggested scheme for numbering the  $\beta$ -amyrin residue (see A) is given. M.p. are corr. H. W.

## VI.—HETEROCYCLIC.

**Production of furfuraldehyde from D-lyxose and D-ribose.** R. C. Hockett, A. Gutttag, and M. E. Smith (*J. Amer. Chem. Soc.*, 1943, **65**, 1—3).—The amounts and rates of production of furfuraldehyde produced from D-lyxose (I) and D-ribose (II) by 12% HCl under standard conditions are recorded. Yields are D-xylose > (II) > L-arabinose > (I). Rates are (II) > (I). R. S. C.

**Furyl ketones.**—See B., 1943, II, 146.

**Rearrangement of phenyl allyl ethers.** VIII. Ethyl *p*- $\gamma$ -dimethylallyloxybenzoate. W. M. Lauer and O. Moe (*J. Amer. Chem. Soc.*, 1943, **65**, 289—293; cf. A., 1943, II, 194).—*p*-OH- $C_6H_4$ -CO<sub>2</sub>Et (I),  $CMe_2CH_2CH_2Br$ , and  $K_2CO_3$  in boiling  $CO_2Me_2$  give an ester (76%), hydrolysed by KOH-MeOH to *p*- $\gamma$ -methyl- $\Delta^2$ -butenoxybenzoic acid (II), m.p.  $150\text{--}151^\circ$ . With aq.  $KMnO_4$  this gives *p*-CO<sub>2</sub>H- $C_6H_4$ -O-CH<sub>2</sub>-CO<sub>2</sub>H and with  $H_2$ -Pd-CaCO<sub>3</sub> gives *p*-CH<sub>2</sub>Bu $\beta$ - $C_6H_4$ -CO<sub>2</sub>H, m.p.  $141\text{--}142^\circ$ , also obtained from (I) by  $CH_2Bu\beta Br$ - $K_2CO_3$ - $CO_2Me_2$  and then KOH-MeOH. The Et ester (prep. by way of the Ag salt), b.p.  $92.5\text{--}93^\circ/0.1$  mm., of (II) at  $197\text{--}224^\circ/50$  mm. gives  $CMe_2CH_2$  (I), and, by "abnormal" rearrangement, after hydrolysis, 1:1:2-trimethyl-1:2-dihydrobenzofuran-4-carboxylic acid (III), m.p.  $180\text{--}182^\circ$  (*p*-bromophenacyl ester, m.p.  $105\text{--}106^\circ$ ). *o*-OMe- $C_6H_4$ -COMe (IV), b.p.  $115\text{--}117^\circ/10\text{--}12$  mm., with  $MgPr\beta Br$  gives  $\beta$ -*o*-anisyl- $\gamma$ -methyl-*n*-butan- $\beta$ -ol, b.p.  $90\text{--}91^\circ/1$  mm., dehydrated by  $H_2SO_4$  in AcOH at room temp. to  $\beta$ -*o*-anisyl- $\gamma$ -methyl- $\Delta^2$ -butene, b.p.  $77\text{--}78^\circ/1$  mm. [with  $CrO_3$ -AcOH gives (IV) and  $CO_2Me_2$ ], which with 48% HBr in boiling AcOH yields 1:1:2-trimethyl-1:2-dihydrobenzofuran, b.p.  $62\text{--}63^\circ/1$  mm. With  $Ac_2O$ - $AlCl_3$  in  $PhNO_2$  at  $<10^\circ$  this gives 4-acetyl-1:1:2-trimethyl-1:2-dihydrobenzofuran, b.p.  $140\text{--}142^\circ/4\text{--}5$  mm. (semicarbazone, m.p.  $186\text{--}187^\circ$ ; with  $PhCHO$ -alkali gives the 4- $CHPh$ : $CH$ : $CO$  derivative, m.p.  $108\text{--}109^\circ$ ), oxidised by  $NaOCl$ -aq. MeOH at  $>48^\circ$  to (III) (proof of structure), m.p.  $182\text{--}183^\circ$ . Replacement of  $K_2CO_3$ - $CO_2Me_2$  in the prep. of (II) by  $NaOEt$ -EtOH leads to 1:1-dimethylchroman-5-carboxylic acid, m.p.  $176\text{--}177^\circ$  (*p*-bromophenacyl ester, m.p.  $147\text{--}148^\circ$ ), also obtained from (I) by  $CMe_2CH_2$  and  $ZnCl_2$  in AcOH at room temp. and later  $\sim 40^\circ$ . R. S. C.

**Preparation of  $\alpha\beta$ -unsaturated aldehydes.**—See A., 1943, II, 195.

**Addition of dienes to coumarin and substituted cinnamic acids.** I. R. Adams, W. D. McPhee, R. B. Carlin, and Z. W. Wicks (*J. Amer. Chem. Soc.*, 1943, **65**, 356—360).— $(CH_2CHMe)_2$  (I), but not  $(CH_2CH)_2$  (II) or isoprene (III), adds to coumarin in xylene at  $260^\circ$  to give 4':5'-dimethyl-1':2':3':6'-tetrahydro-3:4:5:6-dibenz-2-pyrone (22%), m.p.  $181\text{--}181.5^\circ$ , also obtained from *trans*-*o*-OH- $C_6H_4$ -CH:CH-CO<sub>2</sub>H in xylene at  $185^\circ$  and dehydrogenated by Pd-C-CO<sub>2</sub> at  $280\text{--}320^\circ$  to 4':5'-dimethyl-3:4:5:6-dibenz-2-pyrone (IV) (71%), m.p.  $175\text{--}175.5^\circ$ . *cis*-*o*-OMe- $C_6H_4$ -CH:CH-CO<sub>2</sub>H (V) (modified prep.; 93% yield) and (I) in xylene at  $170^\circ$  give 2'-methoxy-4:5-dimethyl-1:2:3:6-tetrahydrodiphenyl-2-carboxylic acid, m.p.  $191^\circ$ ; an isomeride (VI), m.p.  $159\text{--}159.5^\circ$ , is obtained from *trans*-*o*-OMe- $C_6H_4$ -CH:CH-CO<sub>2</sub>H (VII) at  $180^\circ$ ; both products with boiling 48% HBr-AcOH give the same 2'-OH-acid, m.p.  $183\text{--}185^\circ$ , which could not be dehydrated and which loses CO<sub>2</sub> when dehydrogenated and thus has the CO<sub>2</sub> and *o*-OH- $C_6H_4$  in the *trans* configuration. With 48% HBr-AcOH at  $180^\circ$  or KOH-EtOH at  $225^\circ$ , (VI) gives a diastereoisomeric 4':5'-dimethyl-1':2':3':6'-tetrahydro-3:4:5:6-dibenz-2-pyrone, m.p.  $154\text{--}155^\circ$ , and thence (IV). Commercial or pure (III) in xylene with (V) at  $170^\circ$  or (VII) at  $185^\circ$  gives rather poorly 2'-methoxy-5-(or 4)-methyl-1:2:3:6-tetrahydrodiphenyl-2-carboxylic acid, forms, m.p.  $199\text{--}199.5^\circ$  or  $147\text{--}147.5^\circ$ , respectively. (II) does not add to (V) or (VII). 4:6-Dimethoxy-2-methylcinnamic acid, m.p.  $190^\circ$ , is obtained from 7-hydroxy-5-methylcoumarin by boiling NaOH-Me<sub>2</sub>SO<sub>4</sub> in 18% yield or from 3:5:1:2-(OMe)<sub>2</sub> $C_6H_2Me$ -CHO by  $CH_2(CO_2H)_2$ - $C_5H_5N$ -piperidine at  $100^\circ$  in 100% yield; with (I) or (II) in xylene

at  $170^\circ$  it gives 2':4'-dimethoxy-4:5:6'-trimethyl-, m.p.  $174\text{--}175^\circ$ , or -6'-methyl-, m.p.  $140\text{--}141^\circ$ , -1:2:3:6-tetrahydrodiphenyl-2-carboxylic acid, respectively. M.p. are corr. R. S. C.

**Identity of laguncurin, kino-yellow, and maclurin.** M. Nierenstein (*Quart. J. Pharm.*, 1943, **16**, 11—12).—Laguncurin and kino-yellow (obtained by heating aromodendrin above its m.p.) when acetylated ( $Ac_2O$  +  $NaOAc$ ) both yield 5:7-diacetoxy-4-(3':4'-diacetoxyphenyl)coumarin, thus identifying both as maclurin. J. N. A.

**Pyrrolidines and piperidines.**—See B., 1943, II, 145, 174.

**Reaction of glutarimides with phosphorus pentachloride. New pyridine synthesis.** W. W. Crouch and H. L. Lochte (*J. Amer. Chem. Soc.*, 1943, **65**, 270—272).— $[CH_2]_5NH$  and  $PCl_5$  at  $50^\circ$  give 2:3:6-trichloropyridine, m.p.  $66\text{--}67^\circ$  (cf. Bernheimer, A., 1882, 1189), hydrogenated (Pd-C; MeOH-HCl) to  $C_5H_5N$  and probably identical with a substance prepared by Sell *et al.* (*J.C.S.*, 1898, **73**, 439).  $CH_2:CM_2CO_2Me$  (I),  $CN\cdot CH_2\cdot CO_2Et$  (II), and  $NaOEt$  in boiling EtOH give  $CO_2H\cdot CH(CN)\cdot CH_2\cdot CHMe\cdot CO_2Me$ , which at  $220^\circ$  gives CO<sub>2</sub> and  $CN\cdot[CH_2]_2\cdot CHMe\cdot CO_2Me$ , b.p.  $157\text{--}160^\circ/58$  mm., converted by boiling 50%  $H_2SO_4$  and then 25% NaOH into  $CO_2H\cdot[CH_2]_2\cdot CHMe\cdot CO_2H$ , m.p.  $75\text{--}76^\circ$ . The derived anhydride (prep. by  $AcCl$ ) with  $NH_3$  at  $120^\circ$  and then  $200^\circ$  gives  $\alpha$ -methylglutarimide, m.p.  $91^\circ$ , converted by  $PCl_5$  (3 mols.) into 2:5:6-trichloro-2-methylpyridine, m.p.  $94\text{--}95^\circ$ . Condensation of (I) and (II), methylation, hydrolysis, etc. as above give  $\alpha\alpha'$ -dimethylglutarimide, m.p.  $172\text{--}174^\circ$ , and thence by  $PCl_5$  2:6-dichloro-3:5-dimethylpyridine, m.p.  $97\text{--}98^\circ$ . R. S. C.

**Simplified synthesis of nicotinamide and the reaction of hydrogen peroxide with nitriles.** A. Georg and P. Bachmann (*Helv. Chim. Acta*, 1943, **26**, 358—362).—A very poor yield of nicotinamide (I) is obtained by the action of 90%  $H_2SO_4$  on 3-cyanopyridine (II) at  $125^\circ$ . Treatment of (I) with  $H_2O_2$  in feebly alkaline solution at  $65^\circ$  gives (II) in max. yield  $\sim 19\%$ . The yield of (II) increases with  $[H_2O_2]$  to  $\sim 6\%$ , after which it declines. H. W.

**Derivatives of pyridine acids.** I. *N*- $\beta$ -Acylaminoethylnicotinamides. E. M. Hodnett and V. E. Stewart (*J. Amer. Chem. Soc.*, 1943, **65**, 254—255).—Et nicotinate and  $NH_2[CH_2]_2NHAcyl$  at  $100^\circ$  give nicotin- $\beta$ -acet-, m.p.  $170\text{--}171^\circ$ , -propion-, m.p.  $126\text{--}127^\circ$ , -*n*-butyr-, m.p.  $157\text{--}159^\circ$ , -*n*-valer-, m.p.  $141\text{--}142^\circ$ , and -*n*-hexamidoethylamide, m.p.  $124\text{--}125^\circ$ . The products are convulsant stimulants, less toxic than nikethamide but deficient in potency. R. S. C.

**Synthesis of nicotinuric acid.** S. W. Fox and H. Field, jun. (*J. Biol. Chem.*, 1943, **147**, 651—652).—Nicotinamide is converted by  $N_2H_4\cdot H_2O$  in boiling, conc. aq. solution into nicotinhydrazide, m.p.  $158\text{--}159^\circ$ , converted into the azide, m.p.  $48\text{--}49^\circ$ , which with aq.  $NH_2\cdot CH_2\cdot CO_2Na$  affords nicotinuric acid (nicotinylglycine), m.p.  $238\text{--}241^\circ$  (decomp.). H. W.

**Vitamin B group.** II. H. von Euler, L. Ahlström, and H. Hasselquist (*Arkiv Kemi, Min., Geol.*, 1942, **15**, B, No. 21, 8 pp.).—Nicotinyl chloride (I) (hydrochloride used) (1 mol.) and  $CO(NH_2)_2$  (2 mols.) in  $C_5H_5N$  give nicotinylcarbamide, m.p.  $229^\circ$  (decomp.). Acetylsulphanilhydrazide and (I) in  $C_5H_5N$  at  $90\text{--}110^\circ$  afford  $N^1$ -nicotinyl- $N^4$ - (II), m.p.  $197^\circ$  (+ $H_2O$ ), or (6 days at  $100^\circ/12$  mm.) anhyd., m.p.  $235^\circ$  [hydrochloride, m.p.  $239^\circ$ ;  $Ac_2O$  gives the  $N^1$ -Ac derivative,  $C_{18}H_{16}O_5N_4S$ , m.p.  $208^\circ$  (decomp.)], and  $N^1$ -dinicotinyl- $N^4$ -acetylsulphanilhydrazide (III), + $H_2O$ , m.p.  $197^\circ$ , or (2 days at  $110^\circ/12$  mm.) anhyd., m.p.  $208^\circ$  (dihydrochloride, m.p.  $220^\circ$ ). (II) is also obtained from nicotinhydrazide and *p*-NHAc- $C_6H_4$ -SO<sub>2</sub>Cl- $C_5H_5N$  at  $90\text{--}110^\circ$ , whilst (I) and (II) in  $C_5H_5N$  at  $100^\circ$  afford (III). (II) and 10% HCl-EtOH give  $N^1$ -nicotinylsulphanilhydrazide, m.p.  $209^\circ$ . A. T. P.

**Nicotinamide-nucleoside.** F. Schlenk and H. von Euler (*Arkiv Kemi, Min., Geol.*, 1941, **14**, A, No. 13, 12 pp.; cf. A., 1935, 1024).—The isolation of nicotinamide-nucleoside,  $C_{11}H_{15}O_6N_2Cl$ , + $H_2O$  (hydrochloride) (nicotinamide: pentose :: 1.03:1), from phosphatase and cozymase in  $H_2O$  + 0.1N-NaOH at pH 4—5 at  $30^\circ$  for 3—4 days is described. A. T. P.

**Pyridines.**—See B., 1943, II, 146.

**Mesityl oxide and diacetone alcohol in the Bucherer synthesis of hydantoins.** H. R. Henze, T. R. Thompson, and R. J. Speer (*J. Org. Chem.*, 1943, **8**, 17—28; cf. A., 1942, II, 271; Marsh *et al.*, A., 1940, II, 289).—In consequence of divergent results the behaviour of mesityl oxide (I) and diacetone alcohol (II) towards a solution of KCN and  $(NH_4)_2CO_3$  in 50% EtOH (Bucherer procedure for hydantoin formation) has been re-examined. Under these conditions (I) passes at  $58^\circ$  into 5-methyl-5- $\beta$ -methylpropenylhydantoin (III), m.p.  $194^\circ$  (corr.), and 5-hydroxy-3:5:5-trimethylpyrrolidin-2-one (IV), m.p.  $209\text{--}210^\circ$  (corr.) (acetate, m.p.  $138^\circ$ ). (IV) is obtained in 7% yield from diacetoneamine and HCN at  $0^\circ$  followed by treatment of the product with boiling HCl or in 28% yield from diacetoneamine H oxalate and KCN in  $H_2O$  at room temp. with subsequent boiling of the product with HCl. The structure of (III) is established by its hydrogenation to 5-methyl-5-isobutylhydantoin, m.p.  $144.5^\circ$  (corr.), also obtained by treating  $COMeBu\beta$  with KCN

and  $(\text{NH}_4)_2\text{CO}_3$  in 50% EtOH at 58°. Gradual addition of Br in AcOH to a cold solution of (III) in AcOH gives the *dibromide*, m.p. 185° (decomp.). (III) and HBr in AcOH give 5-methyl-5- $\beta$ -bromo- $\beta$ -methylpropylhydantoin (V), m.p. 193° (decomp.), which is converted into (III) by treatment with 0.24N-NaOH at 100°, with AgOH in  $\text{C}_6\text{H}_6$  at 100°, or with aq. NaOAc at room temp. for 3 days. (II) is transformed by prolonged warming with KCN and  $(\text{NH}_4)_2\text{CO}_3$  in 50% EtOH at 58° into 5:5-dimethylhydantoin (VI), m.p. 175—176° (corr.), and  $\alpha$ -hydroxy- $\alpha$ -dimethyl- $\gamma$ -valerolactone (VII), m.p. 65° (corr.), converted into (IV) by treatment NaNO<sub>2</sub>-HCl followed by NaOH; removal of unchanged (VII), and boiling the filtrate with acid. The yields depend considerably on the duration of the heating. Diacetone alcohol cyanohydrin and  $(\text{NH}_4)_2\text{CO}_3$  in EtOH at 58° yield (VI) and  $\alpha$ -ureido- $\alpha$ -dimethyl- $\gamma$ -valerolactone (VIII), m.p. 209—210° (corr.), also obtained by the Bucherer synthesis from (II). (VIII) is converted by boiling  $\text{H}_2\text{SO}_4$  or HCl into  $\alpha$ -carbamido- $\alpha$ -dimethyl- $\gamma$ -valerolactone, m.p. 203° (decomp.), but is unchanged by  $\text{SOCl}_2$  at 100°.  $\alpha$ -Amino- $\alpha$ -dimethyl- $\gamma$ -valerolactone, HCl, and KCNO at 0° give 5-methyl-5- $\beta$ -hydroxy- $\beta$ -methylpropylhydantoin (IX), m.p. 147° (corr.), also obtained from (VIII). (IX) and HBr in AcOH afford (V).  $\text{SOCl}_2$  transforms (IX) into (III). H. W.

**Configuration of trivalent nitrogen. A dicyclic hydrazine derivative.** E. L. Buhle, A. M. Moore, and F. Y. Wiselogle (*J. Amer. Chem. Soc.*, 1943, **65**, 29—32).—Adding  $\text{Br} \cdot [\text{CH}_2]_3 \cdot \text{Br}$  (or  $\text{Cl} \cdot [\text{CH}_2]_3 \cdot \text{Cl}$ ; no details) (1 mol.) slowly to  $\text{N}_2\text{H}_4$  (2 mols.) in boiling 95% EtOH gives bases, separated by fractionation into *pyrazolidine* (I), m.p. 10—12°, b.p. 54—56°/26 mm., 138°/760 mm. (oxalate,  $\text{B}_2\text{H}_2\text{C}_2\text{O}_4$ , m.p. 114—115°;  $\text{Bz}_2$  derivative, m.p. 146—147°), 1:2-trimethylene-pyrazolidine (II), m.p. 1.5—2.5°, b.p. 74—75°/26 mm., 173°/760 mm. (hygroscopic hydrochloride and methiodide; *picrate*, m.p. 159—159.5°), bistrimethylenedi-imine, b.p. 70—73°/15 mm. [7%; *picrate*, m.p. 220—230° (decomp.);  $\text{Bz}_2$  derivative, m.p. 185—186°; *di-oxalate*, m.p. 170—170.5°; *dihydrobromide*, m.p. 240—250° (decomp.) (varies with rate of heating)] (cf. Howard *et al.*, A., 1899, i, 750), and 50% of quaternary salts; the proportions of (I) and (II) formed vary but their combined yield is constantly 30%. (I) reduces Fehling's and Tollens' solutions rapidly at room temp. (II) reduces warm Fehling's solution and cold Tollens' reagent, decolorises Br in  $\text{CCl}_4$ , is indifferent to  $\text{H}_2$ -catalyst, and titrates as a monoacidic base in  $\text{H}_2\text{O}$  ( $K = 1.0 \times 10^{-6}$ ). R. S. C.

**Sulphilimines derived from sulphanilamide.**—See A., 1943, II, 186.

**Pyrazolones.**—See B., 1943, II, 176.

**Action of aliphatic diazo-compounds on  $\alpha\beta$ -unsaturated ketones.**  
**II. *cis*- and *trans*-Dibenzoyl ethylene. III. Benzylideneacetone and diazomethane.** L. I. Smith and K. L. Howard (*J. Amer. Chem. Soc.*, 1943, **65**, 159—164, 165—166; cf. A., 1937, II, 380).—II. *trans*-(CHBz)<sub>2</sub> and  $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O}-\text{CHCl}_3$  at -10° give 99.6% of 3:4-dibenzoyl- $\Delta^1$ -pyrazoline (I), m.p. 108°, but *cis*-(CHBz)<sub>2</sub> gives 3:4-dibenzoyl- $\Delta^2$ -pyrazoline (II) (79.5%), m.p. 129—129.5°. Melting (I) or recrystallising it from aq. EtOH gives (II), which is differentiated from (I) by yielding with PhNCO the 1-carbanilido-derivative, m.p. 156—156.5°. No CO<sub>2</sub> derivatives, NO-derivatives, or reduction products could be obtained from (II). Slow addition of Br in  $\text{CHCl}_3$  to (II) in  $\text{CHCl}_3$  at  $\geq 12^\circ$  and then evaporation in air yields HBr and 3:4-dibenzoylpyrazole (69.3%), m.p. 169°, also obtained from (II) in poor yield by pyrolysis (best at 138—141°/20—24 mm.) or (25%; m.p. 169—170°) by oxidation ( $\text{KMnO}_4$ ; boiling  $\text{COMe}_2$ ).  $\text{CPh}_2\text{N}_2$  and *trans*-(CHBz)<sub>2</sub> in  $\text{CHCl}_3$ -light petroleum give 4:5-dibenzoyl-3:3-diphenyl- $\Delta^1$ -pyrazoline (III) (47.3%), softens 147°, m.p. 157°, 2:3-dibenzoyl-1:1-diphenylcyclopropane (IV) (20.3%), m.p. 179°, and tars; *cis*-(CHBz)<sub>2</sub> reacts more slowly, giving traces of (III) and a substance, m.p. 151—152°, with mainly orange gums. PhNCO, Br, and chloranil do not yield definite products from (III), but  $\text{KMnO}_4$  in  $\text{COMe}_2$  at room temp. yields (IV); pyrolysis, best at 175°/20—21 mm., gives (IV) and (?) 3:4-dibenzoyl-5:5-diphenyl- $\Delta^2$ -pyrazoline, m.p. 173—173.5°. Adding  $\text{NaNH}_2$  to  $\text{COPh}_2 + \text{COPhMe}$  in  $\text{Et}_2\text{O}$  at 0° gives  $\text{CPh}_2(\text{CH}_2\text{Bz})_2$ , converted by Br in  $\text{CS}_2$  at 0° into  $\text{CPh}_2(\text{CHBrBz})_2$  (30%), m.p. 132—133° (and a high-melting by-product), which with KI-EtOH gives (IV). Reduction of (IV) gave gums; the expected products could not be obtained by HBr-AcOH or  $\text{H}_2\text{SO}_4$ -AcOH, and boiling alkaline  $\text{KMnO}_4$ ,  $\text{CHNa}(\text{CO}_2\text{Et})_2$ , and *l*-menthyl *N*-aminocarbamate are without action.  $\text{CHPhN}_2$  and *trans*-(CHBz)<sub>2</sub> give oils.

III.  $\text{CHPh} \cdot \text{CH} \cdot \text{COPh}$  and  $\text{CH}_2\text{N}_2$  in dry  $\text{Et}_2\text{O}$  at -5° to 0° give 3-acetyl-4-phenyl- $\Delta^2$ -pyrazoline (V) (98.8%), m.p. 101° (oxime, m.p. 181°) (cf. Azzarello, A., 1905, i, 941), but in one experiment a small amount of a very unstable substance, m.p. 90—92°, resolidifies, remelts 98—100°, possibly the  $\Delta^1$ -pyrazoline, was obtained. At 190—205°/16—20 mm., (III) gives  $\beta$ -phenyl- $\Delta^2$ -*n*-propenyl Me ketone (46%; 7.5% formed at 230—235°/1 atm.), b.p. 132—138°/17 mm. (semicarbazone, m.p. 183.5—184°), which is unstable in air and with  $\text{O}_3$  in  $\text{CHCl}_3$ , and then Zn dust-AgNO<sub>3</sub>-quinol yields  $\text{COPhMe}$ . R. S. C.

**Pyrazole compounds. II. Synthesis of 3-hydroxy-1-phenyl-5-pyrazoloneimide.** A. Weissberger and H. D. Porter (*J. Amer. Chem.*

*Soc.*, 1943, **65**, 52—54; cf. A., 1943, II, 72).—Adding  $\text{CN} \cdot \text{CH}_2 \cdot \text{COCl}$  (unstable; prep. by  $\text{PCl}_3 \cdot \text{Cl}_2$ ; 54% yield), b.p. 56—58°/0.5 mm., to  $\text{NHPh} \cdot \text{NH}_2$  (I) in  $\text{Et}_2\text{O}$  at 0° gives *cyanoacet- $\beta$ -phenylhydrazide* (II) (33%), m.p. 105—106°. Diazotising  $\text{CN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$  gives the explosive hydrazide (and, by slow reaction, also 16% of *s-di-cyanoacethydrazide*, m.p. 194—196°), which with (I) gives 52% of (II). Adding  $\text{K}_2\text{S}_2\text{O}_8$  to (II) and *p*- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$  in 3% aq.  $\text{Na}_2\text{CO}_3$  gives a yellow-orange colour, discharged by acid. With  $\text{Ac}_2\text{O}$  at 100°, (II) gives  $\alpha$ -acet-, m.p. 149—150°, and with  $\text{BzCl}$ -dioxan at 100° gives  $\alpha$ -benz-, m.p. 155—156°,  $\beta$ -cyanoacet- $\alpha$ -phenylhydrazide, both stable to cold 2% NaOH. In boiling  $\text{NaOMe}$ -MeOH or, less well, cold 2% aq. NaOH, (II) yields 3-hydroxy-5-imino-1-phenylpyrazoline (74%), forms, m.p. 142—143° (stable) and 160.5—161.5°, converted by dil. HCl at 100° into 3-hydroxy-1-phenyl-5-pyrazolone (~20%), also obtained (71%) from 3-amino-1-phenyl-5-pyrazolone by hot HCl-EtOH- $\text{H}_2\text{O}$ . R. S. C.

**Pyrazoles.**—See B., 1941, II, 203.

**Influence of peptide bond glycine in formation of new peptide linkings.** G. Ågren (*Arkiv Kemi, Min., Geol.*, 1941, **14**, B, No. 21, 6 pp.).—The property of  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$  to form anhydrides (diketopiperazines) is transferred to the alanine ester by coupling the latter in peptide linkings with glycine. A comparison is made between rate of anhydride formation of the Et esters of glycine, glycyglycine, diglycyglycine, glycyalanine (I), and alanylglycine (II) in aq. solutions at 37°. Rate of anhydride formation is independent of the initial concn. of the ester and is probably a first-order reaction. In 2 hr., 85% of ester (I) and 64% of (II) are converted into anhydride. A. T. P.

**Reactions of phenanthraquinone and retenequinone with amines under pressure.** G. M. Jaffe and A. R. Day (*J. Org. Chem.*, 1943, **8**, 43—51).—Phenanthrenequinone (I) and  $\text{NH}_2\text{Me}$  in  $\text{C}_6\text{H}_6$  at 100° afford small amounts of phenanthroxazine (II), m.p.  $>360^\circ$ , and of a quinhydrone compound,  $\text{C}_{26}\text{H}_{19}\text{O}_3\text{N}$ , m.p. 150—214° (decomp.), from (I) and 9:10-aminophenanthrol, oxidised entirely to (I) by  $\text{CrO}_3$ , and mainly (63% yield) 1-methylphenanthriminazole, m.p. 196° (*picrate*, m.p. 288—289°). Under similar conditions (I) and  $\text{NH}_2\text{Et}$  afford (II), a quinhydrone, and 2-methyl-1-ethylphenanthriminazole, m.p. 193.5—194.5° [*picrate*, m.p. 222—242° (decomp.)].  $\text{NH}_2\text{Bu}^a$  similarly gives (II), a quinhydrone, and 2-*n*-propyl-1-*n*-butylphenanthriminazole, m.p. 199—200° (*picrate*, m.p. 59—62°).  $\text{CH}_2\text{Ph} \cdot \text{NH}_2$  gives (II), a quinhydrone, m.p. 150—192° (decomp.), and 2-phenylphenanthroxazole, m.p. 206.5—207°. Mechanisms are suggested. Retenequinone and the primary amine in  $\text{C}_6\text{H}_6$  at 100° give exclusively 2-methyl-, m.p. 108°, 2-ethyl-, m.p. 127.5—128.5°, 2-propyl-, m.p. 100—101.5°, and 2-phenyl-, m.p. 172°, -retenoxazole. Aminolysis and simultaneous aminolysis and hydrolysis of 2-arylphenanthroxazoles does not yield iminazoles, thus eliminating the possibility of intermediate oxazole formation in the prep. of iminazoles. H. W.

**Reactions of phenanthraquinone and retenequinone with aldehydes and ammonium acetate in acetic acid solution.** E. A. Steck and A. R. Day (*J. Amer. Chem. Soc.*, 1943, **65**, 452—456).—Formation of iminazoles from phenanthra- (I) or retene-quinone (II) by  $\text{RCHO} \cdot \text{NH}_4\text{OAc} \cdot \text{AcOH}$  occurs by way of the quinonedi-imines. (I) does not react with  $\text{NH}_2\text{Ac}$  or  $\text{CHPh}(\text{NHAc})_2$ , m.p. 254° (lit. 238°), in boiling AcOH, and  $(\text{CHPh})_3\text{N}_2$  is unstable in AcOH. With  $\text{NH}_4\text{OAc}$  in boiling AcOH, (I) gives *phenanthraquinonedi-imine*, +4AcOH, m.p. 243—244°, +3AcOH (retained at 120°), m.p. 240—250°, and solvent-free, m.p. 290—292° ( $\text{Ac}_2$  derivative, m.p. 259—260°, prepared by  $\text{Ac}_2\text{O} \cdot \text{AcOH}$ ), which with PhCHO in boiling AcOH, boiling NaOH-EtOH, or hot piperidine gives 2-phenylphenanthriminazole, m.p. 314° (*picrate*, m.p. 289—290°), also obtained directly from (I) by  $\text{PhCHO} \cdot \text{NH}_4\text{OAc} \cdot \text{AcOH}$ . With  $\text{RCHO} \cdot \text{NH}_4\text{OAc} \cdot \text{AcOH}$ , (I) gives *phenanthriminazole* [4:5-*oo'*-diphenyleneglyoxaline] [prepared by using  $(\text{CH}_2)_3\text{N}_4$  in place of  $\text{RCHO}$ ], m.p. 292°, and its 2-*Pr*<sup>h</sup>, m.p. 228—229°, 2-2'-furyl, + $\text{H}_2\text{O}$ , m.p. 279.5—280.5°, 2-*o*-(+0.5 $\text{H}_2\text{O}$ ), m.p. (anhyd.) 287—287.5° (lit. 270—276°), 2-*m*-, m.p. 343—344°, and 2-*p*-OH- $\text{C}_6\text{H}_4$ , m.p.  $>360^\circ$ , 2-*o*-, m.p. 214—215° (lit. 207—208.5°), and 2-*p*-anisyl, m.p. 254—255°, 2-*m*-, m.p. 271.5—272° (lit. 240°), and 2-*p*-NO<sub>2</sub>- $\text{C}_6\text{H}_4$ , m.p. 341°, 2-*o*- $\text{C}_6\text{H}_4\text{Cl}$ , m.p. 235—235.5°, 2-*p*-NMe<sub>2</sub>- $\text{C}_6\text{H}_4$ , m.p. 259—260°, and 2-3':4'-CH<sub>2</sub>O<sub>2</sub>- $\text{C}_6\text{H}_3$  derivative, m.p. 257—257.5°. Similarly, (II) gives *reteneiminazole*, + $\text{H}_2\text{O}$ , m.p. 128—132°, resolidifies, remelts 167—168°, and its 2-*Ph* derivative, +AcOH, m.p. 93—100°, but with *o*-OH- $\text{C}_6\text{H}_4 \cdot \text{CHO} \cdot \text{NH}_4\text{OAc} \cdot \text{AcOH}$  gives 2-*o*-hydroxyphenylreten-oxazole (65%), m.p. 243—244°, and -iminazole (32%), m.p. 216—217°; the di-imine, which could not be isolated, was probably an intermediate, although (II) and  $\text{NH}_4\text{OAc}$  in boiling AcOH give a substance,  $\text{C}_{18}\text{H}_{19}\text{ON}$ , m.p. 211—220° (*picrate*, m.p. 226—227°), unchanged by PhCHO. M.p. are corr. R. S. C.

**2-Bromo-4:5-dinitrobenzoic acid.**—See A., 1943, II, 192.

**Ultra-violet absorption spectra of nitrogenous heterocycles. V. Blocking effect of methyl groups on the ultra-violet absorption spectra of hydroxypurines and pyrimidines.** J. R. Loofbourow

(Srs.) M. M. Stimson, and M. J. Hart. **VI.** Effect of pH on the spectrum of uracil-5-carboxylic acid. **VII.** Effect of hydroxy-substitutions on the ultra-violet absorption of the series: hypoxanthine, xanthine, and uric acid. (Srs.) M. M. Stimson and M. A. Reuter (*J. Amer. Chem. Soc.*, 1943, 65, 148—151, 151—152, 153—155; cf. A., 1931, 1308).—V. Comparison of the absorption spectra of the pairs uracil-1 : 3-dimethyluracil and xanthine-caffeine shows that the unmethylated compounds exist as ketones until the pH becomes high. Results of Levene *et al.* (A., 1926, 1260) for uracil (I) are confirmed for pH 3—11. pH has a slight effect on the spectra of the methylated compounds, "resonance" (tautomerism),  $\cdot\text{C}^+(\text{O})\cdot\text{C}^-\cdot\text{CH}_2\cdot \rightleftharpoons \cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot \rightleftharpoons \cdot\text{C}(\text{OH})\cdot\text{C}\cdot\text{CH}\cdot$  and  $\cdot\text{NMe}\cdot\text{CH}\cdot\text{N}\cdot \rightleftharpoons \cdot\text{NMe}\cdot\text{C}^-\cdot\text{N}^+\cdot\text{H}\cdot$ , being suggested as the cause.

**VI.** Introduction of  $\text{CO}_2\text{H}$  at  $\text{C}_{15}$  of (I) shifts the weakest absorption of the band at 2700—2900 Å. from pH 11 to pH 7. Absorption at 2170 Å. is due to the  $\text{CO}_2\text{H}$ .

**VII.** Absorption spectra of the hypoxanthine (II), xanthine (III), and uric acid (IV) are reported for pH 3, 7, and 11. At pH 7 each OH shifts the max. 200 Å. towards the red and increases the mol. extinction by 1000 units. (II) shows a drop at pH 7 preliminary to enolisation. (III) resembles (I) in showing enolisation only at pH 11. Since the absorption of (IV) resembles the alkaline absorption of (III), (IV) is probably mono-enolic even in acid. R. S. C.

**Protoporphyrin. L** Purification of protoporphyrin IX as obtained from haemoglobin. **II.** Improved micro-method for converting protoporphyrin into mesoporphyrin. M. Grinstein and C. J. Watson (*J. Biol. Chem.*, 1943, 147, 667—669, 671—673).—I. Crude protoporphyrin is purified by dissolution in  $\text{C}_5\text{H}_5\text{N}$  and addition of light petroleum (I), b.p. 30—60°, to incipient pptn.; separation is nearly quant. if sufficient (I) is used at 0°. Protoporphyrin Me ester, m.p. 223—224°, is obtained by chromatography on  $\text{Al}_2\text{O}_3$  with  $\text{CHCl}_3$ —(I) as eluent. It is best hydrolysed by overnight contact with 25% HCl at 0°.

**II.** Modifications in the method of Fischer *et al.* (A., 1924, i, 230) and Schultze (A., 1942, III, 394) improve the yield of mesoporphyrin to ~60%. H. W.

**Reactions of morpholinomethanol with compounds containing active hydrogen atoms.** M. Zief and J. P. Mason (*J. Org. Chem.*, 1943, 8, 1—6).—Addition of the requisite nitro-paraffin to a mixture of 37%  $\text{CH}_2\text{O}$  and morpholine at 0° gives  $\beta$ -nitro- $\alpha$ -dimorpholino-, m.p. 119—120°, and  $\beta$ -nitro- $\alpha$ -dimorpholino- $\beta$ -methyl-, m.p. 124—125°, -propane and  $\beta$ -nitro- $\alpha$ -morpholinobutane (I), b.p. 134—136°/15 mm. (picrate, m.p. 120—122°). These substances are reduced readily in a Parr hydrogenation apparatus of the low-pressure type using a Raney Ni catalyst activated by the method of Covert and Adkins and 96% EtOH, thus giving  $\beta$ -amino- $\alpha$ -dimorpholino-, m.p. 67—68° (phenylcarbamide, m.p. 233—234°), and  $\beta$ -amino- $\alpha$ -dimorpholino- $\beta$ -methyl-, b.p. 148—150°/1 mm. (phenylcarbamide, m.p. 177—178°), -propane and  $\beta$ -amino- $\alpha$ -morpholinobutane, b.p. 102—104°/14 mm. (3 : 5-dinitrobenzoate, m.p. 162—163°; gummy products with  $\text{PhNCO}$  and  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{NCO}$ ; waxy Bz derivative; does not give Ac or  $p$ - $\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2$  derivatives). Of these  $\text{NO}_2$ -derivatives only (I) appears to be reducible by Sn and HCl. Morpholinomethanol (II) does not appear to react with  $o$ - or  $p$ - $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$  and the product of its reaction with 1 : 2 : 4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$  explodes when distillation is attempted. (II) is transformed by the necessary primary or sec. amine and anhyd.  $\text{K}_2\text{CO}_3$  at room temp. into morpholinomethyl-butylamine, b.p. 58—62°/13 mm., -aniline, b.p. 108—112°/10 mm., - $o$ -toluidine, b.p. 107—109°/10 mm., -diethylamine, b.p. 86—89°/13 mm., -dibutylamine, b.p. 134—136°/14 mm., -dicyclohexylamine, b.p. 112—116°/8 mm., -piperidine, b.p. 111—113°/12 mm., and -morpholine, b.p. 122—124°/12 mm.  $\text{NHPHMe}$  and (II) gave a mixture from which no homogeneous compound other than dimorpholinomethane could be isolated.  $\text{NPhMe}_2$  and (II) do not appear to react. Picrates of these methylenediamines could not be obtained owing to the hydrolysis caused by 96% EtOH. (II) does not appear to react with MeCN, EtCN, or PrCN but with  $\text{CH}_2\text{Ph}\cdot\text{CN}$  yields  $\alpha$ -morpholinomethyl- $\alpha$ -tolunitrile, b.p. 103—105°/7 mm., in 51% yield.  $\text{CH}_2\text{Ph}\cdot\text{COMe}$  and (II) give the compound,  $\text{C}_{18}\text{H}_{28}\text{O}_2\text{N}_2$ , b.p. 109—111°/11 mm., which does not give a picrate. Phenylidimorpholinomethane, m.p. 101—101.5°, is formed from (II) and PhCHO at room temp. H. W.

**Sulphanilamide compounds. VII.** Thiazoline derivatives. J. H. Hunter and H. G. Kolloff (*J. Amer. Chem. Soc.*, 1943, 65, 156—159; cf. A., 1941, II, 147).— $p$ - $\text{NHAcyl}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$  and 2-amino- $\Delta^2$ -thiazoline hydrobromide (I) in aq.  $\text{Na}_2\text{CO}_3$ — $\text{Et}_2\text{O}$  give 2-imino-3- $\text{N}^4$ -acetyl-, m.p. 183°, and 3- $\text{N}^4$ - $n$ -hexoyl-, m.p. 160—160.5°, -sulphanilylthiazolidine, hydrolysed by dil.  $\text{H}_2\text{SO}_4$  at 100° to  $\text{NH}_2$  and 3-sulphanilylthiazolid-2-one (II), m.p. 209—210°. Similarly are prepared 2-imino-3- $\text{N}^4$ -acetylsulphanilyl-4-methyl-, m.p. 178—179°, -5-methyl-, m.p. 162—163°, and -5-phenyl-thiazolidine, m.p. 181—183°, 2-imino-3- $\text{N}^4$ - $n$ -hexoylsulphanilyl-4-methyl-, m.p. 145—146°, -5-methyl-, m.p. 164—165°, and -5-phenyl-thiazolidine, +EtOH, m.p. 203—204°, and thence by hydrolysis 3-sulphanilyl-4-methyl- (III), m.p. 134.5—135.5°, -5-methyl- (IV), m.p. 190.5—191.5°, and -5-phenyl-thiazolid-2-one (V), m.p. 168—170°.  $p$ - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$  with (I) etc. yields 2-imino-3- $p$ -nitrobenzenesulphonyl-thiazolidine (VI),

m.p. 135—137°, -4-, m.p. 133—134.5°, and -5-methylthiazolidine, m.p. 114—114.5°, and -5-phenylthiazolidine, m.p. 139.5—140.5°, with smaller amounts of 2- $p$ -nitrobenzenesulphonimido-3- $p$ -nitrobenzenesulphonyl-thiazolidine, m.p. 268.5—270.5°, -4-, m.p. 242—242.5°, and -5-methylthiazolidine, m.p. 219.5—220.5°, and -5-phenylthiazolidine, m.p. 215.5—218°. Sn-HCl-aq. EtOH at 45—47° reduces (VI) etc. to 2-imino-3-sulphanilyl-thiazolidine (VII), m.p. 144—145°, -4-, m.p. 137—138°, and -5-methylthiazolidine, m.p. 153—153.5°. Dil.  $\text{H}_2\text{SO}_4$  at 100° hydrolyses (VI) etc. to 3- $p$ -nitrobenzenesulphonyl-thiazolid-2-one (VIII), m.p. 182—183°, -4-, m.p. 139—141°, and -5-methylthiazolid-2-one, m.p. 177°, and -5-phenylthiazolid-2-one, m.p. 165.5—168°, respectively. Acid hydrolysis of (VII) etc. also affords (II), (III), and (IV). Preliminary results show the compounds (VIII) etc. to be the most effective of these products against  $\beta$ -haemolytic streptococci, although ineffective against type I pneumococci. R. S. C.

**Thiazoles.**—See B., 1943, II, 174, 175, 178, 199.

**Cyanine dyes.**—See B., 1943, II, 174.

**Isosteric and structurally similar compounds. XVII.** Derivatives of pyrimidinethiazole. H. Erlenmeyer and H. P. Furger (*Helv. Chim. Acta*, 1943, 26, 366—368).—Monobromobarbituric acid and  $\text{HCS}\cdot\text{NH}_2$  in boiling  $\text{Et}_2\text{O}$  give 2' : 6'-diketo-1' : 2' : 3' : 6'-tetrahydropyrimidino-5' : 4'-5 : 4-thiazole,  $\text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{S} \searrow \text{CR}$  [(I), R = H], decomp. 305—310°. 2' : 6'-Diketo-2-methyl-1' : 2' : 3' : 6'-tetrahydropyrimidino-5' : 4'-5 : 4-thiazole [(I), R = Me], decomp. 247°, is obtained similarly from  $\text{MeCS}\cdot\text{NH}_2$  in boiling EtOH. H. W.

## VII.—ALKALOIDS.

**Spectroscopic detection of the opium alkaloids.** P. Csokán (*Z. anal. Chem.*, 1942, 124, 344—351).—Extinction curves are reproduced, and band max. tabulated. L. S. T.

**Aconite alkaloids. XI.** Action of methyl-alcoholic sodium hydroxide on atisine, isoatisine, and dihydroatisine. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1943, 147, 567—569; cf. A., 1942, II, 335).—The conversion of atisine (I) into dihydroatisine (II), m.p. 149—151° softens at 142°,  $[\alpha]_D^{27} - 44^\circ$  in PhMe, is confirmed by analysis of the hydrochloride (III), m.p. 259° (decomp.) after softening, and by the observation that (II) or (III) absorbs 1  $\text{H}_2$  (PtO<sub>2</sub> in MeOH) with production of a mixture of isomerides from which tetrahydroatisine (IV), m.p. 172—173°,  $[\alpha]_D^{25} - 10^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , can be isolated. Milder treatment of (I) with NaOH-MeOH leads to isoatisine (V),  $\text{C}_{22}\text{H}_{33}\text{O}_2\text{N}$ , m.p. 150—151°,  $[\alpha]_D^{25} - 16.5^\circ$  in PhMe [hydrochloride (VI), m.p. 295—299° (decomp.) after softening,  $[\alpha]_D^{25} - 4^\circ$  in  $\text{H}_2\text{O}$ ]. (V) or (VI) absorbs 2  $\text{H}_2$ , giving a mixture from which (IV) is obtained. H. W.

**Aconite alkaloids. XII.** Benzoylheteratisine, a new alkaloid from *Aconitum heterophyllum*. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1943, 147, 571—572; cf. A., 1942, II, 335).—Extraction of atis root with dil.  $\text{H}_2\text{SO}_4$  and treatment of the neutralised ( $\text{Na}_2\text{CO}_3$ ) extract with  $\text{C}_6\text{H}_6$  removes benzoylheteratisine (I),  $\text{C}_{22}\text{H}_{33}\text{O}_2\text{N}$ , m.p. 213—214° after softening,  $[\alpha]_D^{25} + 73^\circ$  in EtOH [hydrochloride, m.p. 218—221° (decomp.) after darkening and softening], hydrolysed to BzOH and heteratisine, m.p. 265—267° (slow decomp.),  $[\alpha]_D^{25} + 40^\circ$  in MeOH, which possibly does not occur as such in *A. heterophyllum* but is an artefact produced from (I) during the isolation process. H. W.

## VIII.—ORGANO-METALLIC COMPOUNDS.

**Relative reactivities of organo-metallic compounds. XLVI.** Addition of metals to phenylated olefines in liquid ammonia solution. H. Gilman and J. C. Bailie. **XLVII.** Organo-strontium compounds. H. Gilman, R. N. Meals, G. O'Donnell, and L. Woods (*J. Amer. Chem. Soc.*, 1943, 65, 267—268, 268—270).—XLVI.  $\text{CPh}_2\cdot\text{CH}_2$  with Na in  $\text{NH}_3$  and then  $\text{NH}_4\text{Cl}$  gives  $\text{CHPh}_2\cdot\text{Me}$  (67%) and  $(\text{CH}_2\cdot\text{CHPh}_2)_2$  (17%) (cf. Wooster *et al.*, A., 1934, 762); with Ca 45—70 and 14%, with Sr 20 and 14%, and with Ba 70 and 35%, respectively, were obtained.  $\text{CPh}_2\cdot\text{CHPh}$  with Ca, Sr, and Ba in  $\text{NH}_3$  gives 40, 61, and 48%, respectively, of  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{Ph}$ .  $\text{CHPh}_3$  with Ba in  $\text{NH}_3$  and then  $\text{CO}_2$  gives only a trace of  $\text{CPh}_3\cdot\text{CO}_2\text{H}$ .

**XLVII.**  $\text{SrEt}_2$  (prep. from  $\text{ZnEt}_2$  and Sr in  $\text{C}_6\text{H}_6$ ) is a highly reactive compound. With  $\text{CPh}_2\cdot\text{CH}_2$  it gives  $\text{Sr}(\text{CPh}_2\text{Pr}^a)_2$ , converted by  $\text{CO}_2$  into  $\text{CPh}_2\text{Pr}^a\cdot\text{CO}_2\text{H}$  (20%). With PhOMe it gives, after treatment with  $\text{CO}_2$ ,  $o$ -OMe- $\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , with dibenzfuran or dibenzthiophen gives the 1-carboxylic acid, with 1- $\text{C}_{10}\text{H}_7\text{Br}$  gives  $\text{Sr}(\text{C}_{10}\text{H}_7\text{I})_2$  and thence  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$ , with  $\text{CO}_2$  gives  $\text{EtCO}_2\text{H}$ , and with PhCN gives  $\text{COPhEt}$ . R. S. C.

**Relative reactivities of organo-metallic compounds. XLV.** Colour test for some highly reactive organo-metallic compounds. H. Gilman and L. A. Woods. **XLVIII.** Direct thallation of dibenzfuran. H. Gilman and R. K. Abbott, jun. (*J. Amer. Chem. Soc.*, 1943, 65, 33—34, 122—123; cf. A., 1942, II, 337).—XLV. Development of a red colour on addition to  $\text{CH}_2\text{Ph}\cdot\text{NH}_2$  or  $\text{NH}(\text{CH}_2\text{Ph})_2$  (I) in light

petroleum distinguishes reactive from unreactive organo-metallic compounds (cf. Krabbe *et al.*, *Ber.*, 1941, **74**, 1343). Examples of reactive compounds are Li, Na, K, LiR [R = Me, Et, Bu<sup>a</sup>, *n*-C<sub>10</sub>H<sub>23</sub>, C<sub>6</sub>H<sub>11</sub>, Ph, *p*-C<sub>6</sub>H<sub>4</sub>Cl, *p*-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>, 2 : 3 : 6 : 1-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>], LiNMe<sub>2</sub>, NaR (R = *n*-amyl, *n*-C<sub>18</sub>H<sub>37</sub>, CH<sub>2</sub>Ph, Ph), KEt, 1 : 8-disodiobenzofuran, SrEt<sub>2</sub>, BaEt<sub>2</sub>, and BaPh<sub>2</sub>, and of unreactive compounds are Ca, Sr, Ba, MgMeCl, MgRBr (R = Me, Et, Ph), CH<sub>2</sub>Ph·MgCl, CoEt<sub>2</sub>, CaBu<sup>a</sup>I, CaPhI, and ZnEt<sub>2</sub>. Colours are given more slowly by *dl*-CHPhMe·NH<sub>2</sub>, Ph·[CH<sub>2</sub>]<sub>x</sub>·NH<sub>2</sub> (*x* = 2 or 3), CH<sub>2</sub>:CH·CH<sub>2</sub>:NH<sub>2</sub>, NH(CH<sub>2</sub>:CH:CH<sub>2</sub>)<sub>2</sub>, NH<sub>2</sub>Ph, β-C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>, or *p*-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub>, but not by N(CH<sub>2</sub>Ph)<sub>3</sub>, NMe<sub>2</sub>·CH<sub>2</sub>Ph, NH<sub>2</sub>Me, NH<sub>2</sub>Bu<sup>a</sup>, NHMe<sub>2</sub>, NHEt<sub>2</sub>, NH<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·OH, NHPMe, or *p*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>. Treating (I) with LiBu<sup>a</sup> in Et<sub>2</sub>O and then with CO<sub>2</sub> gives 2-carboxydibenzylamine, m.p. 164.5—165.5° (preheated at 150—155°) [lactam, m.p. 89—90°, formed at 140°; oxidised by KMnO<sub>4</sub>-KOH to *o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>], intermediates being LiN(CH<sub>2</sub>Ph)<sub>2</sub> and then CH<sub>2</sub>Ph·NLi·CHPhLi.

XLVIII. Dibenzofuran and TiCl<sub>3</sub> in H<sub>2</sub>O-N<sub>2</sub> at 110° and later 165° give Ti<sub>2</sub>Cl<sub>3</sub> and *tl bis*-1-dibenzfuryl chloride (9%), converted by I in CHCl<sub>3</sub> into TII and 1-iododibenzofuran (38%). R. S. C.

## IX.—PROTEINS.

**Nature of peptones.**—See A., 1943, III, 400.

**Purification of tomato bushy stunt and tobacco mosaic viruses.**—See A., 1943, III, 441.

**Inactivation of tomato bushy stunt virus by heating and freezing. Ultracentrifugal examination.**—See A., 1943, III, 441.

**Proteins of tuberculin.** (Miss) F. B. Seibert and J. W. Nelson (*J. Amer. Chem. Soc.*, 1943, **65**, 272—278).—Electrophoresis shows presence in tuberculin of a slow protein having mol. wt. ~32,000 and a faster one having mol. wt. ~16,000. Both have immunological specificity, but the former is more potent as a tuberculin and more antigenic. Immunising rabbits with the larger protein causes sensitisation to the protein and to "old tuberculin" and the presence of antibodies in the γ-component of the sera. The smaller protein may cause antibodies to appear with α-globulin (or albumin). R. S. C.

## X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

**Hydrogenation of tutin.** S. N. Slater (*J.C.S.*, 1943, 143—144; cf. A., 1943, II, 117).—Bromohydro-tutin, C<sub>15</sub>H<sub>17</sub>O<sub>6</sub>Br, m.p. 260° (decomp.), and -picrotoxinin, C<sub>15</sub>H<sub>15</sub>O<sub>6</sub>Br, m.p. 254—255° (decomp.), are obtained by hydrogenation (Pd-C; EtOH) of tutin (I) and picrotoxinin (II), respectively. (I) with H<sub>2</sub>-PtO<sub>2</sub>-AcOH at atm. pressure gives α-dihydrotutin, m.p. 224—226° (decomp.), whilst (II) similarly yields α-dihydropicrotoxinin, m.p. 253—254° (decomp.). Hydrogenation (Pd-C) of (I) in EtOH gives β-dihydrotutin, m.p. 232—233° (decomp.). A. T. P.

**Seeds of *Alangium lamarki*, Thwaites. Isolation of alangol.** P. N. Bhargava and S. Dutt (*Proc. Indian Acad. Sci.*, 1942, **16**, A, 328—331).—Extraction of the kernels with C<sub>6</sub>H<sub>6</sub> yields 0.05% of a sterol, alangol, C<sub>42</sub>H<sub>83</sub>O<sub>6</sub>(OH), m.p. 296° [acetate, m.p. 265° (shrinks at 256°); benzoate, m.p. 276°; phenylurethane, m.p. 242°; digitonide, m.p. 270—273°]. A. L.

## XI.—ANALYSIS.

**Displacement development in adsorption analysis.**—See A., 1943, I, 187.

**Semi-micro-Kjeldahl apparatus.**—See A., 1943, I, 187.

**Semi-micro-determination of sulphur in organic substances.** J. H. Jones (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 182—186).—The combined S in non-volatile org. compounds is oxidised to SO<sub>4</sub><sup>2-</sup> with HNO<sub>3</sub> + HCl + HClO<sub>4</sub>. Tetrahydroxybenzoquinone is used as indicator in the subsequent titration with BaCl<sub>2</sub>. Sulphonol is not quantitatively oxidised in this way. A. A. E.

**ψ-Saccharin chloride, a reagent for identification of alcohols.** J. R. Mead and E. E. Reid (*J. Amer. Chem. Soc.*, 1943, **65**, 457—458).—ψ-Saccharin chloride with ROH at 100° (lower aliphatic R), 125° (sec. or higher primary R), or 125—140° (R = Ar) gives the Me, m.p. 182°, Et, m.p. 219°, Pr<sup>a</sup>, m.p. 124.5°, Bu<sup>a</sup>, m.p. 96°, *n*-amyl, m.p. 62°, *n*-hexyl, m.p. 60°, *n*-C<sub>7</sub>H<sub>15</sub>, m.p. 55°, *n*-C<sub>8</sub>H<sub>17</sub>, m.p. 46°, *n*-nonyl, m.p. 49°, *n*-decyl, m.p. 47.5°, *n*-C<sub>11</sub>H<sub>23</sub>, m.p. 58.5°, *n*-C<sub>12</sub>H<sub>25</sub>, m.p. 54°, *n*-C<sub>13</sub>H<sub>27</sub>, m.p. 66°, *n*-C<sub>14</sub>H<sub>29</sub>, m.p. 62°, *n*-C<sub>15</sub>H<sub>31</sub>, m.p. 72°, *n*-C<sub>16</sub>H<sub>33</sub>, m.p. 69.5°, *n*-C<sub>17</sub>H<sub>35</sub>, m.p. 76°, *n*-C<sub>18</sub>H<sub>37</sub>, m.p. 74.5°, *n*-C<sub>19</sub>H<sub>39</sub>, m.p. 80.5°, Pr<sup>β</sup>, m.p. 137°, Bu<sup>β</sup>, m.p. 100°, sec.-Bu, m.p. 65.5°, iso-, m.p. 64°, and sec.-amyl, m.p. 38°, β-ethyl-*n*-hexyl, m.p. 53.5°, γ-, m.p. 24°, δ-, m.p. 34°, and ε-methyl-*n*-heptyl, m.p. 53°, δ-octyl, m.p. 10°, CH<sub>2</sub>Ph, m.p. 130°, μ-keto-octadecyl, m.p. 77°, Ph,

m.p. 182°, *o*-, m.p. 163°, *m*-, m.p. 146°, and *p*-tolyl, m.p. 171.5°, thymyl, m.p. 147°, *o*-, m.p. 236°, and *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub> ethers, m.p. 192°. M.p. are corr. and ±0.5°. R. S. C.

**[Detection of] ethylene glycol, propylene glycol, glycerol, and diethylene glycol.** M. Orchin (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 99—101).—One drop of a substance, known to be one of the above, is treated with H<sub>5</sub>IO<sub>6</sub>; org. products are CH<sub>2</sub>O, CH<sub>2</sub>O + MeCHO, CH<sub>2</sub>O + HCO<sub>2</sub>H, and —, respectively. O([CH<sub>2</sub>]<sub>2</sub>·OH)<sub>2</sub> is identified as the bis-3 : 5-dinitrobenzoate, m.p. 150.5—151.5° (corr.). A. A. E.

**Photometric determination of reduced and total ascorbic acid.**—See A., 1943, III, 502.

**Chromogenic reagent for vitamin-C determination.**—See A., 1943, III, 502.

**Colour reaction for methionine.** L. H. Sofin, H. Rosenblum, and R. C. Schultz (*J. Biol. Chem.*, 1943, **147**, 557—559).—Methionine (I) gives a yellow colour with a saturated solution of anhyd. CuSO<sub>4</sub> in conc. H<sub>2</sub>SO<sub>4</sub>. The test is not shown by alanine, arginine (sulphate), aspartic acid, cystine, glutamic acid, glycine, histidine (sulphate), hydroxyproline, isoleucine, leucine, lysine (sulphate), norleucine, phenylalanine, proline, serine, threonine, or valine. Tryptophan gives a bright yellow colour with a slight fluorescence and tyrosine a yellow colour less intense than and of different shade from that given by (I). The reaction is adapted to the determination of (I) in leucine, which enhances the colour and hence must be present in equal amount in the blank and test sample. H. W.

**Raman spectra of sugars.**—See A., 1943, I, 176.

**Separation of carotenes from xanthophylls.**—See A., 1943, III, 540.

**Determination of 2 : 4-diaminophenol.** I. S. Shupe (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 123—125).—An empirical gravimetric method based on the formation of a mixture of OBz derivatives is given, together with microchemical identification tests. A. A. E.

**Colour reactions for stilbæstrol.** T. T. Cocking (*Analyst*, 1943, **68**, 144—146).—Stilbæstrol (I) with an excess of Br in AcOH at 100° (bath) for 1 min. gives an orange solution which when treated successively with EtOH and H<sub>2</sub>O forms a violet colloidal dispersion (prevented by oil), provided free Br (or Cl<sub>2</sub> but not I) is present. The colour is extracted by various org. solvents (*e.g.*, CHCl<sub>3</sub>) giving orange-red solutions which fade rapidly when separated and dried. Reaction is quant. and 1 μg. of (I) in 0.1 ml. of AcOH may be detected colorimetrically. With 0.2 atom (min.) or 4 atoms (max.) of Br in warm AcOH, (I) gives a green colour; this may be used as a rapid colorimetric test. Sucrose interferes but lactone does not; many aldehydes interfere. Neither reaction is given by stilbæstrol diacetate or dipropionate or hexæstrol. Dienæstrol gives both reactions, ψ-stilbæstrol only the violet reaction. S. B.

**[Determination of] barbituric acid derivatives, particularly bromobarbiturates and thiobarbiturates.** L. E. Warren (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 101—107).—Two equally satisfactory extraction methods employing respectively CHCl<sub>3</sub> and 80 vol.-% CHCl<sub>3</sub>-Et<sub>2</sub>O are described. A. A. E.

**Simplified photometric determination of trigonelline.** S. W. Fox, E. W. McNeil, and H. Field, jun. (*J. Biol. Chem.*, 1943, **147**, 645—650).—A simplified method of obtaining relatively highly reproducible results in the determination of trigonelline by alkaline treatment has been evolved. MeOH allows the determination to be carried out in a single phase and decolorisation by C is unnecessary since the blank colour is diminished. Dianisidine condenses to a dye of high sensitivity and is usable without previous removal of SO<sub>4</sub><sup>2-</sup>. Glucose interferes with the determination. H. W.

**Microchemical tests for alkaloids and synthetics.** G. L. Keenan (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 96—99).—The Reinecke salt reagent provides a distinctive and sensitive test for choline; PtCl<sub>4</sub> + NaI is less sensitive. A satisfactory procedure for the HAuCl<sub>4</sub> test for sulphadiazine is given. A. A. E.

**Determination of mercury in phenylmercuric nitrate.** W. P. Chambers (*Quart. J. Pharm.*, 1943, **16**, 6—11).—The B.P. 1932 (4th Addendum) method of assay of HgPh·NO<sub>3</sub> is reviewed and the errors in the method, which lead to high results, are discussed. Determination of Hg by a gravimetric method based on pptn. of HgS from an almost boiling solution of the nitrate in glacial AcOH leads to high and somewhat irregular results, but they are ~2% < those obtained by the official assay. Determinations of Hg by reduction with HCO<sub>2</sub>H, by amalgamation of the Hg with Zn, and by digestion with H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> all give reliable results. Full details of these methods are given. It is suggested that the Zn-amalgamation should be substituted for the official method, since it is reliable, manipulation is easy, and a determination can be carried out in 1 hr. compared with 4 hr. and 2 hr. for the HCO<sub>2</sub>H reduction and digestion methods respectively. J. N. A.

## A., II.—Organic Chemistry

AUGUST, 1943.

## I.—ALIPHATIC.

**Chlorination of methane. Nitration of methane.**—See B., 1943, II, 205.

**Production of ethylene and ethylene chlorohydrin.**—See B., 1943, II, 206.

**Photochemical reactions between vinyl chloride and chlorine or bromine, leading to the formation of  $\alpha\beta$ -trichloroethane and  $\alpha\beta$ -dibromochloroethane.**—See A., 1943, I, 206.

**Synthesis of olefine hydrocarbons by catalytic condensation and dehydration of aliphatic aldehydes.** V. I. Komarevsky and T. H. Kritschewsky (*J. Amer. Chem. Soc.*, 1943, **65**, 547—548).—In presence of  $\text{Cr}_2\text{O}_3$  or, less well,  $\text{Al}_2\text{O}_3$  at 330—365°/20 atm.,  $\text{CH}_2\text{R}\cdot\text{CHO}$  gives  $\text{CH}_2\text{R}\cdot\text{CH}(\text{OH})\cdot\text{CHR}\cdot\text{CHO}$ , dehydrated to  $\text{CH}_2\text{R}\cdot\text{CH}:\text{CHR}\cdot\text{CHO}$ ; at 385—410°/20 atm., decomp. to  $\text{CH}_2\text{R}\cdot\text{CH}:\text{CHR} + \text{CO}$  occurs (cf. A., 1942, II, 127). Complex products are also formed. Presence of  $\text{H}_2$  leads to saturated products. Thus, in presence of  $\text{Cr}_2\text{O}_3$  at 400° ( $\text{N}_2$ )  $\text{EtCHO}$  gives  $\text{CHMe}:\text{CHEt}$  (40%) and  $\text{CHEt}:\text{CMe}\cdot\text{CHO}$  (18.7%);  $\text{Pr}^a\text{CHO}$  at 400° ( $\text{H}_2$ ) gives  $\text{CHEt}:\text{CHPr}^a$  (I) (51%),  $\text{CHPr}^a:\text{CET}\cdot\text{CHO}$  (II) (4%), and  $\text{CHEtBu}^a\cdot\text{CHO}$  (III) (4.9%), at 365° ( $\text{H}_2$ ) gives (I) (35%), (II) (15.5%), and (III) (10.4%), at 360° ( $\text{N}_2$ ) gives (I) (15%) and (II) (45%), and at 330° ( $\text{N}_2$ ) gives (I) (6%), (II) (40.2%), and (III) (8.1%);  $\text{Bu}^a\text{CHO}$  at 400° ( $\text{N}_2$ ) gives  $\text{CHPr}^a:\text{CHBu}^a$  (32%);  $n\text{-C}_5\text{H}_{11}\cdot\text{CHO}$  at 408° ( $\text{H}_2$ ) gives  $\text{CHBu}^a:\text{CH}\cdot\text{C}_5\text{H}_{11-n}$  (39%). In absence of a catalyst,  $\text{Pr}^a\text{CHO}$  is unchanged at 402° ( $\text{H}_2$ ). At 400° in presence of  $\text{Al}_2\text{O}_3$  ( $\text{N}_2$ ),  $\text{Pr}^a\text{CHO}$  gives (I) (17%) and (II) (15%), but in presence of  $\text{Cr}_2\text{O}_3\text{-Ni}$  ( $\text{H}_2$ ) gives (I) (50%) and  $n\text{-C}_7\text{H}_{16}$  (50%).  $\text{EtCHO}$  gives also  $\delta$ -methyl-*n*-heptene (10%), b.p. 112—115°, and  $\text{Pr}^a\text{CHO}$  gives also an undecene (5%). R. S. C.

**Catalytic polymerisation of acetylene. Preparation of vinylacetylene.**—See B., 1943, II, 206.

**Addition of hydrogen fluoride to acetylenic compounds.** A. L. Henne and E. P. Plueddemann (*J. Amer. Chem. Soc.*, 1943, **65**, 587—589).—Combination of HF with low-boiling acetylenes ( $>4$  C) is best (75% yield of difluoride) effected by boiling the acetylene (1 mol.) into HF in a Cu flask at 0°.  $\text{C}_3\text{H}_8$  or  $\text{C}_6\text{H}_{10}$  is best dropped into HF stirred at -50°. Higher acetylenes (1 mol.) are dropped into a solution of HF (5 mols.) in  $\text{Et}_2\text{O}$  or  $\text{COMe}_2$  (1 mol.) at 0° and the mixture is then kept at room temp.; the oxonium compounds,  $\text{Et}_2\text{O}\cdot 2\text{HF}$  and  $\text{COMe}_2\cdot 2\text{HF}$ , are good solvents for the reagents and products but the combined HF is not available for addition; yields are 70—75% for rapid and 85—90% for slow addition; any unsaturated impurity is removed by a further reaction.  $\beta\beta$ -Difluoro-butane, f.p. -117.3°, b.p. 30.92°/10 mm., *n*-pentane, f.p. -93°, b.p. 59.7°/20 mm., *n*-hexane, f.p. -82.5°, b.p. 87.4°/20 mm., *n*-heptane, f.p. -62.2°, b.p. 112.7°/20 mm., and *n*-octane (I), f.p. -53.2°, b.p. 137.5°/20 mm.,  $\text{CF}_2\text{EtPr}^a$ , f.p. -89.3°, b.p. 87.4°/20 mm., and  $\delta\delta$ -difluoro-*n*-octane (II), f.p. -45.9°, b.p. 137.3°/20 mm., are thus prepared.  $\text{CF}_2\text{Et}_2$ , f.p. -94.0°, b.p. 60.2°/20 mm., and *n*-heptylene difluoride, f.p. -82°, b.p. 119.7°/20 mm., are prepared from the corresponding dichlorides. Markovnikov's rule is valid: e.g.,  $\text{CMe}_2\text{C}\cdot\text{C}_5\text{H}_{11}$  gives 87% of (I) and 13% of (II) as determined by the f.p. curve. Further reactive groups in the acetylene often interfere:  $\Delta^{\alpha\theta}$ -nonadi-inene gives  $\beta\beta\theta\theta$ -tetrafluoro-*n*-nonane, f.p. -2.3°/20 mm., b.p. 82°/20 mm., and some  $\beta\theta$ -difluoro- $\Delta^{\alpha\theta}$ -nonadiene, f.p. 1.19°/4 mm., b.p. 87°/20 mm., but  $\Delta^{\alpha\theta}$ -heptadi-inene is completely resinified. Other physical data of the products are recorded. *n* is valuable as a criterion of purity. R. S. C.

**Catalytic decomposition of ethyl alcohol in presence of magnesium oxide.**—See A., 1943, I, 205.

**Condensation of epichlorohydrin with ethylene glycol; new polyfunctional derivatives.** M. S. Kharasch and W. Nudenberg (*J. Org. Chem.*, 1943, **8**, 189—193).—Epichlorohydrin (I) condenses with  $(\text{CH}_2\cdot\text{OH})_2$  in presence of conc.  $\text{H}_2\text{SO}_4$  at room temp. and subsequently at 100° to  $\alpha$ -chloro- $\gamma$ - $\beta'$ -hydroxyethoxypropan- $\beta$ -ol (II), b.p. 135—139°/3 mm. (yield 56%). (II) is transformed by  $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{ONa}$  (III) into  $\alpha\gamma$ -di- $\beta$ -hydroxyethoxypropan- $\beta$ -ol, b.p. 188—192°/2—3 mm., m.p. 30°, more conveniently obtained from (I) and (III).  $\text{KOH-EtOH}$  at 2° transforms (II) into  $\alpha\beta$ -epoxy- $\gamma$ - $\beta'$ -hydroxyethoxypropane (IV), b.p. 92—94°/2 mm., converted by boiling  $\text{H}_2\text{O}$  into  $\gamma$ - $\beta'$ -

hydroxyethoxypropane- $\alpha\beta$ -diol, b.p. 162—164°/3 mm., also obtained from (II) and boiling aq.  $\text{Na}_2\text{CO}_3$ ; this is transformed by paracet-aldehyde and a little 50%  $\text{H}_2\text{SO}_4$  into 2-methyl-4- $\beta$ -hydroxyethoxymethyl-1:3-dioxolen, b.p. 113—115°/8 mm. (IV) is transformed by conc. aq.  $\text{NH}_3$  into  $\alpha$ -amino- $\gamma$ - $\beta'$ -hydroxyethoxypropan- $\beta$ -ol, b.p. 141—144°/2—4 mm., and by  $\text{NHMe}_2$  into the  $\alpha$ - $\text{NMe}_2$ -compound, b.p. 102—105°/1—2 mm. 2-Hydroxymethyl-1:4-dioxan (V), b.p. 92—93°/8 mm., is obtained by treating (IV) with conc.  $\text{H}_2\text{SO}_4$  at room temp. and then at 100°; the 3:5-dinitrobenzoate has m.p. 106—108° (decomp.).  $\text{KOH-EtOH}$  and (II) afford  $\alpha$ -ethoxy- $\gamma$ - $\beta'$ -hydroxyethoxypropan- $\beta$ -ol, b.p. 115—122°/2 mm., and (V).

H. W.

**Dipole moments of derivatives of ethylene glycol and glycerides.**—See A., 1943, I, 193.

**Utilisation of aliphatic nitro-compounds. VIII. Nitrotriols (nitroglycerols) prepared from simple aldehydes.** C. A. Sprang [with E. F. Degering] (*J. Amer. Chem. Soc.*, 1943, **65**, 628).— $\text{NO}_2\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{OH}$  (from  $\text{MeNO}_2$  and  $\text{EtCHO}$ ) (1 mol.), 40% aq.  $\text{CH}_2\text{O}$  (1 mol.), and  $\text{K}_2\text{CO}_3$  in  $\text{EtOH}$  at room temp. give  $\beta$ -nitro- $\beta$ -hydroxymethyl-*n*-pentane- $\alpha\gamma$ -diol, m.p. 141°.  $\beta$ -Nitro- $\beta$ -hydroxymethyl-*n*-hexane-, m.p. 154—156°, *n*-nonane-, m.p. 145—147°, and  $\epsilon$ -methyl-*n*-hexane-1:3-diol, m.p. 144—146°, are similarly prepared. R. S. C.

**Production of isopropyl ether.**—See B., 1943, II, 207.

**Action of polyhalogenated derivatives on organomagnesium compounds.** G. Sanna [in part with S. Spano] (*Gazzetta*, 1942, **72**, 305—312).— $\text{CCl}_3\cdot\text{SCl}$  with  $\text{MgEtBr}$  in  $\text{Et}_2\text{O}$  gives  $\text{CCl}_3\cdot\text{Et}$  sulphide, b.p. 85°/10 mm., and  $(\text{CCl}_3\cdot\text{S})_2$  (I), and with  $\text{MgPhBr}$  gives  $\text{Ph}\cdot\text{CCl}_3$  sulphide, b.p. 135°/10 mm., (I), and  $\text{Ph}_2$ .  $\text{CCl}_3\cdot\text{SO}_2\text{Cl}$  with  $\text{MgEtBr}$  in  $\text{Et}_2\text{O}$  gives  $\text{CCl}_3\cdot\text{Et}$  sulphide and  $\text{CCl}_3\cdot\text{SOEt}$ , and with  $\text{MgPhBr}$  gives  $\text{Ph}\cdot\text{CCl}_3$  sulphide, m.p. 121°, and  $\text{Ph}_2$ . E. W. W.

**Sulphonium compounds. II. Derivatives of nitric and of organic acids.** F. E. Ray and G. J. Szasz (*J. Org. Chem.*, 1943, **8**, 121—125).— $\text{Me}_2\text{S}$  and  $\text{MeNO}_3$  at room temp. slowly afford trimethylsulphonium nitrate (corresponding mono- and di-picrate, m.p. 199° and 70—75° respectively).  $\text{MeEtS}$  and  $\text{MeNO}_3$  give a non-cryst. product transformed into  $\text{SMe}_3$  picrate. Evidence of formation of a sulphonium compound from  $\text{EtNO}_3$  and  $\text{Me}_2\text{S}$  was not obtained.  $\text{SEt}_3\cdot\text{NO}_3$  could not be obtained pure from  $\text{EtNO}_3$  and  $\text{Et}_2\text{S}$  but the product is convertible into  $\text{SEt}_3$  picrate, m.p. 115°; the change is accelerated by  $\text{C}_5\text{H}_5\text{N}$ . Impure  $\text{HCO}_2\text{SMe}_3$  is derived from  $\text{Me}_2\text{S}$  and  $\text{HCO}_2\text{Me}$ .  $\text{Me}$  stearate when heated with  $\text{Me}_2\text{S}$  for 200 hr. at 70° yields some solid and the product affords  $\text{SMe}_3$  dipicrate. No visible change occurs between cottonseed oil and  $\text{Me}_2\text{S}$  but the aq. extract gives a picrate, m.p. 90° to a red liquid. H. W.

**Sulphonation of  $\beta$ -methylallyl chloride. Mobility of the olefinic linking in unsaturated sulphonic acids.** C. M. Suter and F. G. Bordwell (*J. Amer. Chem. Soc.*, 1943, **65**, 507—517).— $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\text{Cl}$  (I) (1.73 mols.) and dioxan,  $\text{SO}_3$  (2.13 mols.) in  $(\text{CH}_2\text{Cl})_2$  at 0° give a solution (A), which with  $\text{NH}_2\text{Ph}$  gives exothermally 20% of  $\text{NH}_2\text{Ph}\cdot\text{H}_2\text{SO}_4$  (II) +  $\text{NH}_2\text{Ph}$  phenylsulphamate (III) (see below) with 80% of mixed monosulphonates; passing  $\text{NH}_3$  into (A) gives similar mixed  $\text{NH}_4$  salts. Purification of the  $\text{NH}_4$  (B) or  $\text{NH}_2\text{Ph}$  (C) salts yields products which give  $\text{AgCl}$  with warm  $\text{AgNO}_3$  but no  $\text{SO}_4^{2-}$  with  $\text{KMnO}_4$  and thus are  $\text{CH}_2\text{Cl}\cdot\text{C}(\text{CH}_2)\cdot\text{CH}_2\cdot\text{SO}_3\text{M}$  (D); crude (B) give ~20% of  $\text{SO}_4^{2-}$  and thus contain  $<25\%$  of  $\text{CH}_2\text{Cl}\cdot\text{CMe}\cdot\text{CH}\cdot\text{SO}_3\text{NH}_4$  (E), and crude (B) or (C) with aq.  $\text{HNO}_3\text{-AgNO}_3$  at 100° give only ~65% of  $\text{AgCl}$ , indicating presence of ~35% of  $\text{CHCl}\cdot\text{CMe}\cdot\text{SO}_3\text{M}$ . The (II) and (III) are derived from  $\beta$ -methyl- $\beta$ -chloromethylethionic anhydride (IV),  $\text{CH}_2\text{Cl}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{O}$  (see below). (B) yield nearly pure benzyl-

thiuronium salts, m.p. 103—105° and 123—128°, derived from (D) and (E), respectively, or vice versa. A 1:1 mixture (F) of  $\text{CH}_2\cdot\text{C}(\text{CH}_2\text{Cl})_2$  and  $\text{CHCl}\cdot\text{CMe}\cdot\text{CH}_2\text{Cl}$  [obtained from (I) by  $\text{Cl}_2$ ] with boiling aq.  $\text{Na}_2\text{SO}_3$  gives  $\text{Na}$   $\alpha$ -chloro- $\beta$ -methyl- $\Delta^{\alpha}$ -propene- $\gamma$ -sulphonate, decomp. 305—310° [and some disulphonate (V)]; with  $\text{NaOH}$ , but not  $\text{AgNO}_3$ , gives  $\text{Cl}^-$ ; with cold  $\text{KMnO}_4$  gives no  $\text{SO}_4^{2-}$ , and thence the benzylthiuronium salt, m.p. 123.5—125°, and, by way of the acid chloride, the amide, m.p. 68—69°. With  $\text{PCl}_5$  or  $\text{POCl}_3$  and then  $\text{Et}_2\text{O-NH}_3$ , (B) give  $\gamma$ -chloro- $\beta$ -methyl- $\Delta^{\alpha}$ -propene- $\alpha$ -sulphonamide, m.p. 75.5—77°, which with  $\text{O}_3$  gives 40% of  $\text{H}_2\text{SO}_4$  but only 2% of  $\text{CH}_2\text{O}$ . With aq.  $\text{Na}_2\text{SO}_3$ , (B) give

salts (VI), converted by  $\text{POCl}_3$  into  $\text{SO}_2\text{Cl}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{SO}_2\text{Cl}$ , m.p. 78—79°, also obtained from (V) by  $\text{PCl}_5$ . The rearrangement occurs during prep. of (V) or (VI), since (a) (V) yields the corresponding dibenzylthiuronium salt, dimorphic, m.p. 139—141° and 158—159°, and (b) with  $\text{O}_3$  gives 69% of  $\text{CH}_2\text{O}$  but only 9% of  $\text{SO}_4^{2-}$ . Rearrangement also occurs during prep. of OPh-derivatives: with PhOH in boiling 33% NaOH, (B) give *Na*  $\alpha$ -phenoxy- $\beta$ -methyl- $\Delta^a$ -propene- $\gamma$ -sulphonate (VII), darkens 340°, decomp. 345—350° (derived benzylthiuronium salt, m.p. 145—146°), also obtained from (IV) by PhOH and NaOH at 100° and from (I) by  $\text{ClSO}_3\text{H}$ , followed by NaOPh. Its structure is proved by oxidation by aq. Br to  $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{OH}$  and failure to give  $\text{SO}_4^{2-}$  with  $\text{KMnO}_4$ . It is partly isomerised in hot AcOH, yielding then  $\text{SO}_4^{2-}$  with  $\text{KMnO}_4$  and  $\text{CH}_2\text{O}$  with  $\text{O}_3$ . With  $\text{K}_2\text{CO}_3$  and PhOH in  $\text{COMe}_2$  and then aq.  $\text{Na}_2\text{SO}_3$ , (F) gives *Na*  $\gamma$ -phenoxy- $\beta$ -methylenepropene- $\alpha$ -sulphonate, dimorphic, m.p. 226—230° (derived benzylthiuronium salt, m.p. 117—118°), which with  $\text{KMnO}_4$  at 0° and then the b.p. gives OPh- $\text{CH}_2\cdot\text{CO}_2\text{H}$ , with  $\text{O}_3$  gives  $\text{CH}_2\text{O}$  (45%), with Br gives  $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{OH}$ , and in hot 10% NaOH rearranges to (VII). With  $\text{SO}_3$  in  $(\text{CH}_2\text{Cl})_2$  at 0°, (I) gives (IV) (50%), m.p. 66—68°, stable at -5° but not at room temp. (vac.), which in  $\text{H}_2\text{O}$  is acidic (litmus), yields  $\text{SO}_4^{2-}$  but not  $\text{Cl}^-$  immediately, and is only slightly unsaturated, but in aq. alkali is highly unsaturated, yielding  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  quantitatively when heated therein. R. S. C.

**Manufacture of formic acid.**—See B., 1943, II, 207.

**Ozonisation of acetic acid and acetic anhydride.** H. Paillard and E. Briner (*Helv. Chim. Acta*, 1942, 25, 1528—1533).—AcOH is very slightly attacked by  $\text{O}_3$  yielding  $\text{AcO}_2\text{H}$ , which in presence of  $\text{H}_2\text{O}$  is decomposed with formation of  $\text{H}_2\text{O}_2$ .  $\text{Ac}_2\text{O}$  is even more slowly attacked. The bluish colour of a solution of  $\text{O}_3$  in AcOH disappears when  $\text{O}_3$  is removed and the ultra-violet absorption spectrum becomes identical with that prior to ozonisation. AcOH is therefore a very suitable solvent for ozonisation reactions. J. W. S.

**Derivatives of aldol and crotonaldehyde. II.  $\alpha$ -Chlorocrotyl acetate.** E. Späth and H. Schmid (*Ber.*, 1940, 73, [B], 243—248).—The product of the action of  $\text{AcCl}$  on  $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$  at 35—40° is identified as  $\alpha$ -chlorocrotyl acetate, b.p. 64—66°/8.5 mm., since it is readily hydrolysed by cold  $\text{H}_2\text{O}$  to  $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$  (identified as the semicarbazone) and converted by ozonisation in EtCl with treatment of the product with  $\text{H}_2\text{O}$  containing Zn dust, quinol, and  $\text{AgNO}_3$  into  $\text{MeCHO}$ ; the yield of  $\text{MeCHO}$  is approx. equal to that obtained under similar conditions from  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{OAc})_2$ .  $\text{Pr}^a\text{CHO}$  and  $\text{AcCl}$  afford  $\alpha$ -chloro-*n*-butyl acetate, b.p. 51—52°/9.5 mm. H. W.

**Preparation and properties of trifluoromethyl compounds.** J. H. Simons and E. O. Ramler (*J. Amer. Chem. Soc.*, 1943, 65, 389—392).— $(\text{CF}_3\cdot\text{CO}_2)_2\text{Ba}$  and boiling  $\text{PCl}_5$  give *trifluoroacetyl chloride* (I) (53%), m.p. -146°, b.p. -27°, and thence the known  $\text{CF}_3\cdot\text{CO}\cdot\text{NH}_2$ .  $\text{PBr}_3$  at 190° gives similarly *trifluoroacetyl bromide* (59.3%), m.p. -136°, b.p. -5°. With  $\text{C}_6\text{H}_5\cdot\text{AlCl}_3$  at  $\sim 5^\circ$ —room temp., (I) yields *trifluoroacetophenone* (43%), m.p.  $\sim -40^\circ$ , b.p. 75°/37 mm., 152°/730 mm., which is sol. in 10% aq. KOH, giving  $\text{BzOH}$  and a gas (?  $\text{CHF}_3$ ), yields a cryst.  $\text{NaHSO}_3$  compound, rapidly gives  $\text{CHF}_3$  if a neutral solvent is present, gives a 2:4-dinitrophenylhydrazone, m.p. 94.5—95.5°, does not give a cyanohydrin, with  $\text{PCl}_5$  at 175° yields  $\beta\beta$ -dichloro- $\alpha\alpha$ -trifluoro- $\beta$ -phenylethane (48.5%), b.p. 89—90° (resistant to  $\text{SbF}_5$ ), and with  $\text{MgPhBr}\cdot\text{Et}_2\text{O}$  gives *diphenyltrifluoromethylcarbinol* (46%), m.p. 74—74.5°, b.p. 157°/17 mm.  $\text{CPhF}_3$  (133), Fe (1 g.), and Br (24 c.c.) at, successively, 60—70°, 56°, and 60° give *m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CF}_3$  (II) (52%), b.p. 151—152°, hydrolysed by boiling 80%  $\text{H}_2\text{SO}_4$  to *m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$ ; use of more Fe leads to 25% of (II) and 8% of 3:4:1- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{CF}_3$ , b.p. 102—104°/25 mm., hydrolysed to 3:4:1- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{CO}_2\text{H}$ . In  $\text{Et}_2\text{O}$ , (II) gives a Grignard reagent (100%), which with  $\text{Me}_2\text{SO}_4\cdot\text{Et}_2\text{O}$  at the b.p. gives  $\text{CPhF}_3$  (65%) and *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CF}_3$  (9.1%), b.p. 127° (hydrolysed to *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ ).  $\text{CF}_3\cdot\text{COI}$  could not be prepared. An excellent yield of  $\text{CPhF}_3$  is obtained from  $\text{CPhCl}_3$  by HF at high temp./>1 atm. F is detected by pptn. by  $\text{Ce}(\text{NO}_3)_3\cdot\text{AcOH}$ . R. S. C.

**Resolution and rates of hydrolysis of *dl*- $\alpha$ -bromopropionic acid and its glycine derivatives.** A. F. Chadwick and E. Pacsu (*J. Amer. Chem. Soc.*, 1943, 65, 392—402).—Yields by resolution of *dl*- $\text{CHMeBr}\cdot\text{CO}_2\text{H}$  (I) by alkaloids are low because of decomp. of the salts. *dl*- $\alpha$ -Bromopropionylglycine ions are equally unstable. *dl*- $\alpha$ -Bromopropionylglycylglycine is resolved by quinine in 0.8% EtOAc solution, yielding a Na salt,  $[\alpha]_D^{20} +27.7^\circ$  in  $\text{H}_2\text{O}$ , and an acid,  $[\alpha]_D^{20} -18.0^\circ$ . The kinetics of the first- and second-order reactions involved in removal of Br from the ions are investigated; mechanisms are discussed. Decomp. of the solid brucine salts is measured; that of (I) yields *dl*-lactylglycinelactone. R. S. C.

**Synthesis of methacrylic acid.** T. White (*J.C.S.*, 1943, 238—239).—By careful control of conditions, Me isopropenyl ketone may be oxidised by strongly alkaline aq. NaOCl to  $\text{CH}_2\cdot\text{CMe}\cdot\text{CO}_2\text{H}$ , the Me ester of which with the appropriate alcohol gives the *ethylene di*-, b.p. 122—126°/15 mm., and the *n*-hexyl esters, b.p. 86—88°/17 mm. F. R. S.

**Normal addition of hydrogen bromide to  $\Delta^a$ -butenoic,  $\Delta^a$ -pentenoic, and  $\Delta^a$ -hexenoic acid in hexane.** A. Michael and H. S. Mason (*J. Amer. Chem. Soc.*, 1943, 65, 683—686).—Mixtures of  $\text{Br}\cdot[\text{CH}_2]_{3-4}\cdot\text{CO}_2\text{H}$  with  $\text{CHMeBr}\cdot[\text{CH}_2]_{2-3}\cdot\text{CO}_2\text{H}$  are analysed by the much faster reaction of the *sec.* bromides with  $\text{AgNO}_3\text{--HNO}_3\text{--H}_2\text{O--EtOH}$  at 27°. When  $\text{O}_2$  and peroxides are rigidly excluded, addition of HBr to  $\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_{1-3}\cdot\text{CO}_2\text{H}$  is 88—100% (in one case 75%) "normal." R. S. C.

**Wandering of halogen atoms in carbon chains and rings. V.** C. D. Nenitzescu, I. G. Gavat, and D. Cocora (*Ber.*, 1940, 73, [B], 233—237).—Addition of  $\Delta^a$ -hexenoic acid (I) in  $\text{C}_6\text{H}_6$  to  $\text{AlCl}_3$  in  $\text{C}_6\text{H}_6$  at 45—50° yields exclusively  $\delta$ -phenylhexoic acid, b.p. 143°/1 mm. (chloride, b.p. 138°/11 mm.; amide, m.p. 75°). Under similar conditions but with  $\text{CS}_2$  as solvent (I) and  $\text{AlCl}_3$  give a mixture of partly halogenated  $\Delta^a$ - and  $\Delta^a$ -acids, converted by hydrolysis followed by ozonisation into some  $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$  but no  $\text{Pr}^a\text{CO}_2\text{H}$ . Migration of the double linking occurs in a direction opposite to that of the classical Fittig reaction. This isomerisation is not general since  $\Delta^1$ -cyclohexenecarboxylic acid is not thus affected.  $\beta$ -Methyl- $\Delta^a$ -hexenoic acid,  $\text{AlCl}_3$ , and  $\text{C}_6\text{H}_6$  give  $\delta$ -phenyl- $\beta$ -methylhexoic acid (II), b.p. 138—140°/1.5 mm. (chloride, b.p. 119°/5 mm.; amide, m.p. 78°).  $\delta$ -Phenylpentan- $\beta$ -ol, b.p. 124—125°/15 mm., obtained by reduction of the corresponding ketone, is converted by  $\text{PBr}_3$  into the corresponding bromide, b.p. 115°/10 mm., which is condensed with  $\text{CH}_2(\text{CO}_2\text{Et})_2$ ; the product is hydrolysed and decarboxylated to (II). Unexpectedly, sorbic acid,  $\text{AlCl}_3$ , and  $\text{C}_6\text{H}_6$  afford (II). H. W.

**Esters of methylnepentylacetic acid.** F. C. Whitmore, J. D. Surmatis, and J. N. Haimsohn (*J. Amer. Chem. Soc.*, 1943, 65, 487).—Et, b.p. 176.8°/734 mm.,  $\text{Pr}^a$ , b.p. 196.6°/734 mm.,  $\text{Bu}^a$ , b.p. 213.8°/734 mm., and *n*-hexyl  $\alpha\gamma\gamma$ -trimethyl-*n*-valerate, b.p. 247.2°/734 mm., are obtained from the acid by  $\text{SOCl}_2$  and then ROH (excess). R. S. C.

**A monomeric aldehyde peroxide (isocarboxylic acid).** H. J. Backer and J. Strating (*Ber.*, 1940, 73, [B], 316—317).—Mainly comment on the work of Rieche *et al.* (A., 1940, II, 63). Previous work (A., 1934, 662; 1935, 498) has shown that 3-*tert*-butyl-2:5-dihydrothiophen 1:1-dioxide gives an ozonide, hydrolysed to an isocarboxylic acid, convertible by alkali into  $\text{CMe}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . A. T. P.

**Fatty acids. XII. Preparation of  $\alpha$ - and  $\beta$ -linoleic acids by debromination in various solvents.** Chemistry of these acids. J. S. Frankel and J. B. Brown (*J. Amer. Chem. Soc.*, 1943, 65, 415—418; cf. A., 1943, II, 151).—The following nomenclature is adopted for linoleic acids: no prefix = the *cis-cis* acid (I) ( $\text{Br}_4$  no. 102.9);  $\alpha$ - the mixture obtained from the tetrabromides (II), m.p. 114—115°;  $\beta$ - product from liquid tetrabromides obtained by brominating (I) or the  $\alpha$ -acid; crystallisation acid = product obtained by crystallising the acids from semi-drying oils; isomeric acids (*cis-trans* or *trans-cis*) = acids giving only liquid tetrabromides.  $\text{Et}_2\text{O}$  is the best solvent for debromination;  $\text{Pr}^a_2\text{O}$  and dioxan are also satisfactory; MeOH leads to Me esters;  $\text{C}_5\text{H}_5\text{N}$  is difficult to remove from the product; AcOH leads to acids of low I val. and  $\text{Br}_4$  no.; light petroleum is useless.  $\text{C}_5\text{H}_5\text{N}$  leads to acids of correct  $\text{Br}_4$  no. but low m.p. In MeOH liquid tetrabromides give only 40—60% of distillable acid, probably owing to polymerisation, but the yield from (II) is nearly quant. Oxidation of the  $\alpha$ -acid gives  $\sim 50\%$  of sativic acids, but little or none is obtained from the  $\beta$ -acid.  $\alpha$ - and  $\beta$ -Acids contain 1.0—1.2 and 1.9—6.4% of conjugated acid. The  $\beta$ - differs from the  $\alpha$ -acid mainly in containing only 15—53% of (I), 32—70% of isomeric acids, and 6—22% of much altered acids. The isomeric acids are not *trans-trans*, since they give no tetrabromide, m.p. 78°. With two samples of  $\beta$ -acid the I val. rises with time, but this is only partly due to conjugation.  $\beta$ -Acid, obtained by debromination in  $\text{C}_5\text{H}_5\text{N}$ , had m.p. -2°. Crystallisation of the  $\beta$ -acid at low temp. has not been effected. R. S. C.

**Heat-polymerisation of triglycerides. I. Tristearin and triolein.** N. L. Phalnikar and B. V. Bhide (*J. Univ. Bombay*, 1943, 11, A, Part 5, 77—82).—Distillation of tristearin at 30 mm. yields stearic acid (58), tristearin (22), and stearone with traces of hydrocarbons (26%), with a negligible residue. Triolein similarly gives nonoic and oleic acids, triolein, and hydrocarbons with a trace of ketones, with a residue yielding on hydrolysis sebacic and oleic acids, and polymerised acid fractions, mol. wt. 553, 443, 539, and 634. In each case much acraldehyde and some  $\text{CO}_2$  are evolved. A. Li.

**Condensations. XIX. Alkylation of  $\beta$ -keto-esters with alcohols and ethers in presence of boron trifluoride.** J. T. Adams, B. Abramovitch, and C. R. Hauser (*J. Amer. Chem. Soc.*, 1943, 65, 552—554; cf. A., 1943, II, 119).—Passing  $\text{BF}_3$  into ROH (1 mol.) or  $\text{R}_2\text{O}$  (0.5 mol.) and  $\text{COR}\cdot\text{CH}_2\cdot\text{CO}_2\text{R}'$  gives  $\text{COR}\cdot\text{CHR}\cdot\text{CO}_2\text{R}'$ ; side-reactions are dehydrogenation of ROH or dealcoholation of  $\text{R}_2\text{O}$  to give olefines (which may polymerise), exchange of  $\text{R}'$  for R, and further reaction of the product. Time and temp. of reaction greatly affect the yield and under suitable conditions the yield of  $\text{CHPr}^a\text{Ac}\cdot\text{CO}_2\text{Et}$  (I), b.p. 97—98°/20 mm., by use of  $\text{Pr}^a\text{OH}$  is

increased to 67% cf. A., 1940, II, 374). Et  $\alpha$ -cyclohexylacetate, b.p. 146—148°/20 mm., is obtained in 32—34% yield and with 5% NaOH gives cyclohexylacetone.  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  (II) with  $\text{Bu}^\gamma\text{OH}$  or  $\text{EtOBu}^\gamma$  (in this and other cases also  $\text{BF}_3$ ) gives 6—14% of  $\text{CHBu}^\gamma\text{Ac}\cdot\text{CO}_2\text{Bu}^\gamma$  (and unsaturated hydrocarbons) and thence  $(\text{H}_2\text{SO}_4\text{--AcOH}) \text{COMe}\cdot\text{CH}_2\text{Bu}^\gamma$  (23%), b.p. 123—126°.  $\text{CMe}_2\text{Et}\cdot\text{OH}$  and (II) give an ester, hydrolysed to  $\text{CMe}_2\text{Et}\cdot\text{CH}_2\cdot\text{COMe}$ .  $(\text{CH}_2\text{Ph})_2\text{O}$  and (II) at  $-70^\circ$  to  $-10^\circ$  give 18% of  $\text{CH}_2\text{Ph}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ , b.p. 164—166°/12 mm.  $\text{CHMeAc}\cdot\text{CO}_2\text{Et}$  and  $\text{Pr}^\beta_2\text{O}$  at  $24^\circ$  give  $\text{CMePr}^\beta\text{Ac}\cdot\text{CO}_2\text{Et}$  (55%), b.p. 98—98.5°/15 mm., and  $\text{COMe}\cdot\text{CHMePr}^\alpha$  (semicarbazone, m.p. 107—107.5°). Alkylation does not occur with (a) (II) and  $\text{Bu}^\alpha\text{OH}$ ,  $\text{Bu}^\beta\text{OH}$ , *sec.*- $\text{BuOH}$ ,  $\text{Et}_2\text{O}$ , or  $\text{Pr}^\beta_2\text{O}$ , (b)  $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$  and  $\text{Pr}^\beta\text{OH}$ ,  $\text{Et}_2\text{O}$ , or  $\text{Pr}^\beta_2\text{O}$ , (c) (I) and  $\text{Pr}^\beta_2\text{O}$ , or (d)  $\text{CH}_2(\text{CO}_2\text{Et})_2$  or  $\text{MeNO}_2$  and  $\text{Pr}^\beta_2\text{O}$  or  $\text{Bu}^\gamma\text{OH}$ ; (II) and  $\text{BuOH}$  give  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{R}$  ( $\text{R} = \text{Bu}^\alpha$  or  $\text{Bu}^\beta$ ). R. S. C.

**Stereochemical relationships of the  $\theta$ -oxidostearic acids and the  $\theta$ -dihydroxystearic acids.** D. Atherton and T. P. Hilditch (*J.C.S.*, 1943, 204—208).—When the two isomeric forms of  $\theta$ -oxidostearic acid are treated with  $\text{Et}_2\text{O}\cdot\text{HCl}$ , chlorohydroxystearic acids are produced which in presence of alkali re-form the original oxido-acid. Hence the inversion, which occurs when either of the  $\theta$ -(OH) $_2$ -acids is converted into the chlorohydroxy-acids and the latter, through the oxido-compounds, into the isomeric form of the (OH) $_2$ -acid, must take place during replacement of OH by Cl. This leads to the conclusion that no inversion takes place during the conversion of oleic and elaidic acid into the  $\theta$ -(OH) $_2$ -acids, m.p. 95° and 132°, respectively, by means of  $\text{BzO}_2\text{H}$ ,  $\text{AcO}_2\text{H}$ , or Caro's acid.

F. R. S.

**Oxidation of resorcinol by hydrogen peroxide in presence of tungstic acid sol as catalyst.** B. C. Kar (*J. Indian Chem. Soc.*, 1942, 19, 499—500).—Oxidation of resorcinol with  $\text{H}_2\text{O}_2$ , in presence of tungstic or molybdic acid sol, gives  $\text{CO}_2$  and maleic acid. The kinetics of the reaction are studied.

A. T. P.

**Autocondensation of oxalacetic acid.** F. L. Breusch and R. Tulus (*Rev. Fac. Sci. Istanbul*, 1942, A, 6, 144—149).—Oxalacetic acid (I) in cryst. form occurs only as the *cis*- and *trans*-enolic modifications but in aq. solution is present also in the keto-form and, under certain conditions, as keto-hydrate (II). This latter form is subject to autocondensation with a second mol. of (I) to products which resemble citric acid and give the  $\text{CBr}_3\cdot\text{CO}\cdot\text{CHBr}_2$  reaction. In conc. aq. solution the production of (II) is favoured by conc. alkalis, in dil. aq. solution by  $\text{Ca}^{++}$ .

H. W.

**Preparation of lower aldonic acids by oxidation of sugars in alkaline solution.** H. S. Isbell (*J. Res. Nat. Bur. Stand.*, 1942, 29, 227—232).—Directions are given for the prep. of *l*-erythronic (I), *d*-threonic (II), *d*-lyxonic, *l*-xylonic, and *d*-arabonic acid (III) by oxidation with  $\text{O}_2$  of the appropriate sugar in alkaline solution. (III) is obtained in ~70% yield in agreement with the results of previous investigators; with the other aldonic acids lower yields are obtained which do not differ greatly from those obtained by oxidation with air. The simplicity of the method is a great recommendation. (I) and (II) are separated as their brucine salts, the optical rotations of which are represented by:  $[\alpha]_D^{20} = -28.4 - 0.85C + 0.025C^2$  in which  $C$  is the g. of anhyd. brucine *l*-erythronate in 100 ml. of aq. solution, and  $[\alpha]_D^{20} = -28.5 - 0.9C + 0.025C^2$  in which  $C$  is the g. of anhyd. brucine *d*-threionate in 200 ml. of aq. solution.

H. W.

**Synthesis of some  $\alpha$ -acyltetronic acids.** W. Baker, K. D. Grice, and A. B. A. Jansen (*J.C.S.*, 1943, 241—242).— $\alpha$ -Acetyltetronanilide (improved prep.) is hydrolysed in cold alkaline solution to  $\alpha$ -acetyltetronic acid (I), which condenses with aldehydes in  $\text{AcOH}$  and a little piperidine in poor yield to give  $\alpha$ -( $\beta'$ -phenylacrylyl)-, m.p. 138—140°,  $\alpha$ -( $\beta'$ -phenylpropionyl)-, m.p. 131°,  $\alpha$ -( $\beta'$ -*p*-anisylacrylyl)-, m.p. 164°,  $\alpha$ -( $\beta'$ -styrylacrylyl)-, m.p. 178—182° [reduced ( $\text{H}_2\text{--Ni}$ ) to  $\alpha$ -( $\delta'$ -phenylvaleryl)-, m.p. 81.5—82.5°], and  $\alpha$ -( $\beta'$ -2-furylacrylyl)-tetronic acid, m.p. 146—148° [reduced to the  $\alpha$ -( $\beta'$ -2-tetrahydrofurylpropionyl)-acid, m.p. 73.5—74°]. The oxime of (I) undergoes the Beckmann transformation ( $\text{PCl}_5\text{--PCl}_3$ ) to  $\alpha$ -acetamidotetronic acid, m.p. 170°.

F. R. S.

**Diethyl acetal of  $\gamma$ -methyl- $\Delta^2$ -butenal.** D. Kritchevsky (*J. Amer. Chem. Soc.*, 1943, 65, 487).— $\text{CH}_2\text{CMe}\cdot\text{CH}_2\cdot\text{MgCl}$  and  $\text{CH}(\text{OEt})_3$  in boiling  $\text{Et}_2\text{O}$  give  $\text{CH}_2\text{CMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$  (24%), b.p. 154—155°, and then  $\beta$ -methyl- $\Delta^2$ -butenaldehyde-*p*-nitro-, m.p. 157°, and -2:4-dinitro-phenylhydrazones, m.p. 181°, and -semicarbazones, m.p. 204—205°.

R. S. C.

**Ultra-violet absorption spectra of tagetone and related ketones.**—See A., 1943, I, 191.

**$\beta$ -Alkylthioethylamines and the corresponding carbamides, sulphoxides, and sulphones.** K. W. Brighton and E. E. Reid (*J. Amer. Chem. Soc.*, 1943, 65, 458—459).—Adding  $\text{RSH}$  and then  $\text{Br}\cdot[\text{CH}_2]_2\cdot\text{NH}_2\cdot\text{HBr}$  to  $\text{NaOEt}\text{--EtOH}$  and then boiling gives  $\beta$ -*n*-butyl-, b.p. 211°,  $\beta$ -*n*-, b.p. 231°, and  $\beta$ -*iso*-amyl-, b.p. 231°,  $\beta$ -*n*-hexyl-, b.p. 252°, and  $\beta$ -*n*-heptyl-thioethylamine, b.p. 270°, which yield their respective hydrochlorides, m.p. 118°, —, 167°, 131°, and 121°, carbamide derivatives, m.p. 91°, 101°, 111°, 99°, and 95°.

sulphoxide hydrochlorides, m.p. 112°, 121°, —, 127°, and 123°, and sulphone hydrochlorides, m.p. 211°, 221°, —, 238°, and 230°.

R. S. C.

**Iron pentacarbonyl as solvent and reaction medium.**—See A., 1943, I, 198.

**High mol. wt. aliphatic compounds of nitrogen and sulphur.** B. A. Hunter (*Iowa State Coll. J. Sci.*, 1942, 17, 85—87; cf. A., 1941, II, 279, 283).—The following have been prepared: *N*-*n*-octadecyl-ammonium nicotinate, m.p. 78—79°, -nicotinamide, m.p. 91—92°, -pyrrole, m.p. 74—75°, 2:5-dimethyl-1-*n*-octadecyl-, m.p. 39—40°, and 1-*n*-dodecyl-pyrrole, b.p. 138—140°/1 mm., 1-*n*-octadecyl-, m.p. 107—108° (*Et* $_2$  ester, m.p. 33—33.5°), and 1-*n*-dodecyl-pyrrole-3:4-dicarboxylic acid (*Et* $_2$  ester, b.p. 240—243°/5 mm.). *n*- $\text{C}_{12}\text{H}_{25}\cdot\text{NH}_2$  with  $\text{HNO}_2$  gives some *n*- $\text{C}_{12}\text{H}_{25}\cdot\text{OH}$  with *n*- $\Delta^2$ - $\text{C}_{12}\text{H}_{24}$ , converted into *n*- $\alpha\beta$ - $\text{C}_{12}\text{H}_{24}\text{Br}_2$ , b.p. 156—158°/6 mm. Nitration of *n*- $\text{C}_{12}\text{H}_{25}\cdot\text{CO}_2\text{H}$  yields presumably *n*- $\alpha$ - $\text{NO}_2\cdot\text{C}_{12}\text{H}_{14}\cdot\text{CO}_2\text{H}$  (*Et* ester, b.p. 150—160°/1 mm.). Contrary to Collin *et al.* (A., 1933, 1141), *n*- $\text{C}_{18}\text{H}_{37}\cdot\text{SH}$  has m.p. 31°. Contrary to the principles of homology, *n*- $\text{C}_{12}\text{H}_{25}\cdot\text{SH}$  with Na yields (*n*- $\text{C}_{12}\text{H}_{25}$ ) $_2\text{S}$ . Fuming  $\text{H}_2\text{SO}_4$  sulphonates *n*- $\text{C}_{17}\text{H}_{35}\cdot\text{CO}_2\text{H}$  at 50° and *n*- $\text{C}_{17}\text{H}_{35}\cdot\text{CN}$ , the Ba salt being isolated in the former case.

F. R. G.

**Action of thionyl chloride on urethanes.** L. C. Raiford and H. B. Freyermuth (*J. Org. Chem.*, 1943, 8, 174—178).—Under the conditions of Warren *et al.* (A., 1935, 854), the production of an allophanate from  $\text{NH}_2\cdot\text{CO}_2\text{Et}$  or  $\text{NH}_2\cdot\text{CO}_2\text{Bu}^\alpha$  (I) could not be confirmed. (I) and  $\text{SOCl}_2$  in boiling  $\text{C}_6\text{H}_6$  afford *Bu* $^\alpha$  allophanate, m.p. 149—150°, with a small amount of cyanuric acid. The action of  $\text{SOCl}_2$  with *N*-aryl-substituted urethanes to give uretediones is sp., as far as tested, for the Ph derivative. Compounds containing "negatively" substituted Ph suffer no change when refluxed with the reagent but tar is formed when the substituent is alkyl.  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}_2\text{Et}$  (II) is slowly transformed by  $\text{SOCl}_2$  at 0° into *Et* 1-chloro-2-naphthylaminoformate, m.p. 94—95°, and *Et* 2-naphthyl-iminochlorosulphinate, m.p. 133—134°, which loses  $\text{SO}_2$  when preserved particularly in sunlight and partly regenerates (II) when boiled with  $\text{EtOH}$ . *Et* 4-chloro-1-naphthylaminoformate, m.p. 143—144°, is obtained similarly from  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ ; it is hydrolysed by  $\text{KOH}\text{--EtOH}$  to 4:1- $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{NHAc}$ , m.p. 97—98°.

H. W.

**Amino-acids and their derivatives. V. Synthesis of  $\alpha$ -amino- $\alpha$ -methylbutyric acid and  $\alpha$ -amino- $\alpha$ -isopropylbutyric acid.** L. Li, K. Lin, Y. Huang, and S. Kang. VI. Synthesis of  $\alpha$ -amino- $\alpha$ -ethylvaleric acid. L. Li, K. Lin, Y. Huang, and A. Y. L. Huang. VII. Synthesis of  $\alpha$ -amino- $\delta$ -methyl- $\alpha$ -isoamylhexoic acid ( $\alpha$ -aminodiisoamylacetic acid). Y. Huang, K. Lin, L. Li, and M. Lu (*J. Chinese Chem. Soc.*, 1942, 9, 1—13, 14—30, 31—40).—V.  $\text{CN}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$  (I) and  $\text{NaOEt}\text{--EtOH}\text{--MeI}$  give  $\text{CN}\cdot\text{CMeEt}\cdot\text{CO}_2\text{Et}$ , b.p. 90.5—94°/18.5 mm., which with conc.  $\text{H}_2\text{SO}_4$  at 37° (50 hr.) affords *Et*  $\alpha$ -carbamyl- $\alpha$ -methylbutyrate, m.p. 46—46.5° [corresponding butyric acid, m.p. 99° (decomp.)]. Bromination in  $\text{CHCl}_3\text{--aq. NaOH}$  at  $-12^\circ$  to  $-15^\circ$  then yields the *N*-Br-derivative, converted by 30% aq.  $\text{KOH}$  at 50—70° into *Et*  $\alpha$ -amino- $\alpha$ -methylbutyrate, b.p. 65—66°/20 mm. (picrate, new m.p. 151.5—152.5°; phenylcarbamyl derivative, m.p. 114°; free butyric acid, m.p. 308°). A product, b.p. 95.5°/13.5 mm., containing 91% of (I), prepared from  $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$  and  $\text{EtBr}\text{--EtOH}$ , reacts with  $\text{Pr}^\beta\text{Br}\text{--NaOEt}\text{--EtOH}$  to give  $\text{CN}\cdot\text{CEtPr}^\beta\cdot\text{CO}_2\text{Et}$ , b.p. 105—108.5°/15 mm., and thence (conc.  $\text{H}_2\text{SO}_4$  at 100° for 25 min.) *Et*  $\alpha$ -carbamyl- $\alpha$ -isopropylbutyrate, m.p. 88°; its *N*-Br-derivative and 30% aq.  $\text{KOH}$  at 60° afford *Et*  $\alpha$ -amino- $\alpha$ -isopropylbutyrate, b.p. 52°/4.3 mm. (hydrochloride, m.p. 136.5—138°). The corresponding butyric acid, m.p. 283° (decomp.), affords a chloroacetyl derivative, m.p. 177.5°, a phenylcarbamyl compound, m.p. 181° (decomp.), and thence 1-phenyl-4-ethyl-4-isopropyl-hydantoin, m.p. 115.5—116.5°.

VI.  $\text{CN}\cdot\text{CHPr}\cdot\text{CO}_2\text{Et}$  and  $\text{Et}\text{--I}\text{--NaOEt}\text{--EtOH}$  give  $\text{CN}\cdot\text{CEtPr}\cdot\text{CO}_2\text{Et}$  (II); pure (II) is converted by conc.  $\text{H}_2\text{SO}_4$  at 100° (bath) into *Et*  $\alpha$ -carbamyl- $\alpha$ -ethylvalerate (III), m.p. 86.5°; aq.  $\text{KOH}$  gives the corresponding acid (IV), m.p. 139.5—140°, also obtained from (II) by 26% aq.  $\text{KOH}$  at 120°, followed by conc.  $\text{H}_2\text{SO}_4$  at 100° (bath). (III) and Br-10% aq.  $\text{NaOH}\text{--CHCl}_3$  at  $-12^\circ$  to  $-15^\circ$  give the *N*-Br-derivative (V), converted by 30% aq.  $\text{KOH}$  at 50—60° into *Et*  $\alpha$ -amino- $\alpha$ -ethylvalerate, b.p. 61°/3.8 mm. (hydrochloride, m.p. 80—86°). (V) with  $\text{NaOMe}\text{--MeOH}$  at room temp. overnight, then at 80°, affords *Et*  $\alpha$ -carbomethoxyamino- $\alpha$ -ethylvalerate (VI), b.p. 92—93.5°/5 mm. Br-MeOH and (IV)- $\text{NaOEt}\text{--EtOH}$  at 0°, followed by  $\text{NaOMe}$ , at room temp. overnight, then at 80°, yield *Me*  $\alpha$ -amino- $\alpha$ -ethylvalerate, b.p. 94°/6.5 mm. (hydrochloride, m.p. 133—134°; phenylcarbamyl derivative, m.p. 122—124°), and some  $\alpha$ -carbomethoxyamino- $\alpha$ -ethylvalerate (VII), m.p. 112° (decomp.) [obtained also from (IV) and Br-MeOH- $\text{NaOMe}$  at 20°].  $\alpha$ -Amino- $\alpha$ -ethylvaleric acid, m.p. 303° (sealed capillary) (chloroacetyl, m.p. 191—192°, carbamyl, decomp. 187—187.5°, and hydantoin derivative, m.p. 145.5—146.5°), is obtained by hydrolysis of its Me or Et ester, by heating the respective hydrochloride with  $\text{Ag}_2\text{CO}_3$ , or by hydrolytic decomp., using aq.  $\text{Ba}(\text{OH})_2$  at 120—125° or 120—140°, of (VI) and (VII), respectively.

VII.  $\text{CN}\cdot\text{C}(\text{CH}_2\text{Bu}^\beta)_2\cdot\text{CO}_2\text{Et}$ , b.p. 157°/16 mm., and conc.  $\text{H}_2\text{SO}_4$  at 100° (bath) give *Et*  $\alpha$ -carbamyl- $\delta$ -methyl- $\alpha$ -isoamylhexoate, m.p.

65—66° (acid, m.p. 140—143°; diisoamylacetamide, new m.p. 118—118.5°), thence the *N*-Br-derivative (VIII), converted by 10% aq. NaOH at 25—30°, then at <20°, into carbethoxydiisoamylmethylcarbamide (IX), b.p. 126.5—127°/5.5 mm. (NH<sub>2</sub>Ph gives the phenylcarbamido-derivative, *Et* α-phenylcarbamido-δ-methyl-α-isoamylhexoate, m.p. 118—119°). (IX) refluxed with fuming HCl yields, through the hydrochloride, m.p. 280—282° (decomp.), α-amino-δ-methyl-α-isoamylhexoic acid (α-aminodiisoamylacetic acid) (X), m.p. 290° (decomp.) [phenylcarbamyl derivative, m.p. 177° (decomp.); chloroacetyl compound, m.p. 153°]. (IX) and α-amino-γ-methyl-α-isobutyl valerate in *N*-NaOH at 70—80° afford *N*-(carboxydiisobutylmethyl)-*N'*-(carbethoxydiisoamylmethyl)carbamide, m.p. 184—185°. (VIII) and NaOMe-MeOH at 80—83° yield *Et* α-carbomethoxyamino-δ-methyl-α-isoamylhexoate, b.p. 132—133°/4.3 mm., hydrolysed by refluxing with aq. Ba(OH)<sub>2</sub> at 120—125° to (X). A. T. P.

**Synthesis of *dl*-serine.** C. E. Redemann and R. N. Icke (*J. Org. Chem.*, 1943, 8, 159—161).—Passage of OH·[CH<sub>2</sub>]<sub>2</sub>·OEt over Cu chromite heated at 310—330° in a vertical Pyrex tube gives OEt·CH<sub>2</sub>·CHO in 30—35% yield. This is converted into *dl*-serine, m.p. 243—244° (decomp.) after darkening at 228° (corr.), by the modified Strecker reaction. H. W.

**Characteristic reaction possibilities of natural compounds containing sulphur.** A. Schöberl (*Angew. Chem.*, 1940, 53, 227—232).—A lecture.

**Aliphatic carbodi-imides. II.** E. Schmidt and W. Striewsky (*Ber.*, 1940, 73, [B], 286—293).—Simplified methods for the prep. of OMe·CH<sub>2</sub>·CNS (I) and OEt·CH<sub>2</sub>·CNS are given. NH<sub>2</sub>Me transforms (I) in Et<sub>2</sub>O into *N*-methyl-*N'*-methoxymethylthiocarbamide, m.p. 76—77°, converted by HgO in dry Et<sub>2</sub>O into methylmethoxymethylcarbodi-imide (II), b.p. 35.5—36.5°/10 mm., which slowly becomes acid when preserved yielding a solid which does not regenerate (II) when distilled. Similar methods are used in the prep. of *N*-methyl-*N'*-ethoxymethyl-, m.p. 83—84°; *N*-methoxymethyl-*N'*-*n*-propyl-, m.p. 58.5—59.5°; *N*-methoxymethyl-*N'*-isopropyl-, needles, m.p. 80.5—81.5°, or, less frequently, plates, m.p. 73—75° when rapidly heated or m.p. 80—81° softens at 73—75° when slowly heated; *N*-ethoxymethyl-*N'*-isopropyl-, m.p. 77—78°; *N*-methoxymethyl-*N'*-isohexyl-, m.p. 35.5—37°; *N*-cyclohexyl-*N'*-methoxymethyl-, m.p. 103—104°, and *N*-cyclohexyl-*N'*-ethoxymethyl-, m.p. 109—110°, -thiocarbamide. These are converted respectively into methylethoxymethyl-, b.p. 46—47°/10 mm.; methoxymethyl-*n*-propyl-, b.p. 61.5—62.5°/10 mm.; methoxymethylisopropyl-, b.p. 52—53°/10 mm.; ethoxymethylisopropyl-, b.p. 62.5—63.5°/10 mm.; methoxymethylisohexyl-, b.p. 97—98°/10 mm.; cyclohexylmethoxymethyl-, b.p. 109—110°/10 mm.; and cyclohexylethoxymethyl-, b.p. 117.5—118.5°/10 mm., -carbodi-imide. H. W.

**Hydrogenation of adiponitrile.**—See B., 1943, II, 209.

**[Manufacture of] unsaturated ether nitriles, cyanoalkyl ethers of monohydric alicyclic alcohols, and cyanoalkyl ethers of ether alcohols.**—See B., 1943, II, 208.

## II.—SUGARS AND GLUCOSIDES.

**Carbohydrate formation in nature.**—See A., 1943, III, 534.

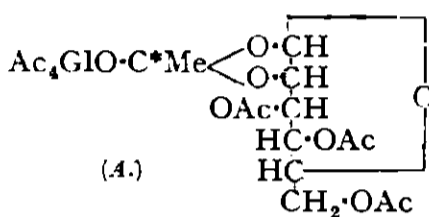
**Lead tetra-acetate oxidations in the sugar group. III.** Triphenylmethyl ethers of β-methyl-*D*-arabinopyranoside and of α-methyl-*L*-fucopyranoside. Determination of their structures. R. C. Hockett and D. F. Mowery, jun. (*J. Amer. Chem. Soc.*, 1943, 65, 403—409; cf. A., 1939, II, 407, 493).—β-Methyl-*D*-arabinopyranoside (I) (0.133) with CPh<sub>3</sub>Cl (0.16 mol.) in C<sub>6</sub>H<sub>5</sub>N at 23° (18 days) gives the 2-CPh<sub>3</sub> ether (II) (40%), m.p. 143—145°, [α]<sub>D</sub><sup>20</sup> −79.7° in EtOH, −75.8° in CHCl<sub>3</sub>, and 2 : 3-(CPh<sub>3</sub>)<sub>2</sub> ether (III) (6%), m.p. 191—192°, [α]<sub>D</sub><sup>20</sup> −81.7° in CHCl<sub>3</sub>, −58.6° in C<sub>6</sub>H<sub>5</sub>N, and a syrup, which with Ac<sub>2</sub>O-C<sub>6</sub>H<sub>5</sub>N at 0° gives the 3-CPh<sub>3</sub> ether 2 : 4-diacetate (IV), m.p. 202—203°, [α]<sub>D</sub><sup>20</sup> −107.6° in CHCl<sub>3</sub>. In boiling NaOMe-MeOH, (IV) gives β-methyl-*D*-arabinopyranoside 3-CPh<sub>3</sub> ether (V), +2MeOH, m.p. 157—159°, [α]<sub>D</sub><sup>20</sup> −103.7° in CHCl<sub>3</sub>, −93.3° in MeOH, which resists the action of Pb(OAc)<sub>4</sub> in C<sub>6</sub>H<sub>5</sub>N (proof of structure). The structure of (II) could not be thus determined, since reaction in C<sub>6</sub>H<sub>5</sub>N is so fast that the difference for β-methyl-*D*-glucopyranoside and (I) is indistinct. AcOH causes perceptible hydrolysis of the CPh<sub>3</sub> ethers, but can be used as solvent for rate determinations if allowance is made for this consumption of reagent; thus, (II) is shown to contain the *cis*-glycol grouping. (III) gives β-methyl-*D*-arabinopyranoside 2 : 3-(CPh<sub>3</sub>)<sub>2</sub> ether 4-acetate, m.p. 193—194°, [α]<sub>D</sub><sup>20</sup> −98.8° in CHCl<sub>3</sub>, [α]<sub>D</sub><sup>25</sup> −109.7° in C<sub>6</sub>H<sub>5</sub>N; when kept in AcOH at 60°, this loses the CPh<sub>3</sub> to give a solution which is attacked by Pb(OAc)<sub>4</sub> at a rate characteristic of *trans*-glycols, thus establishing the structure of (III). CPh<sub>3</sub>·OAc is unaffected by Pb(OAc)<sub>4</sub>-AcOH. CPh<sub>3</sub> is removed from (III) by AcOH at 60° but not from (IV) at room temp. CPh<sub>3</sub>Cl converts (V), but not (II), into (III). 50% of (III) is obtained by using 4 mols. of CPh<sub>3</sub>Cl per mol. of (I). α-Methyl-*L*-fucopyranoside gives 81.5% of the 2-CPh<sub>3</sub> ether, m.p. 127—128° (corr.), [α]<sub>D</sub><sup>20</sup> −58.0° in CHCl<sub>3</sub> (cf. A., 1934, 635) (3 : 4-diacetate, m.p. 208—210°, [α]<sub>D</sub><sup>20</sup> −37.5° in CHCl<sub>3</sub>), the structure of

which is proved as above and confirmed by the similarity of its [M]<sub>D</sub> to that of (II). The OH at C<sub>(2)</sub> is thus the most reactive *sec.* OH. Unless otherwise stated, [α] are [α]<sub>D</sub><sup>20</sup>. R. S. C.

**Mutarotation of β-*D*-altrose.** N. K. Richtmyer and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, 65, 740—741).—β-*D*-Altrose exhibits mutarotation which is very rapid at first (cf. A., 1935, II, 135; also Austin *et al.*, A., 1934, 759). Its initial [α]<sub>D</sub><sup>20</sup> is, by extrapolation, −69°, its final [α]<sub>D</sub><sup>20</sup> +33.1°, in H<sub>2</sub>O. R. S. C.

**Hydrogenation of invertible saccharides.**—See B., 1943, II, 209.

**Synthesis of disaccharide acetates in the mannose series.** E. A. Talley, D. D. Reynolds, and W. L. Evans (*J. Amer. Chem. Soc.*, 1943, 65, 575—582).—Acetobromomannose (I), β-*D*-mannose 1 : 2 : 3 : 4-tetra-acetate, CaSO<sub>4</sub>, Ag<sub>2</sub>O, and I in CHCl<sub>3</sub> give 6-β-*D*-mannosido-6-β-*D*-mannose octa-acetate (39%), m.p. 152—153° (corr.), [α]<sub>D</sub><sup>25</sup> +19.6° in CHCl<sub>3</sub>, which is shown to be the normal form by constancy of [α] in HCl-CHCl<sub>3</sub> and by hydrolysis by NaOMe-MeOH or acid to 6-β-*D*-mannosido-β-*D*-mannose, softens 70°, decomp. 90—95° (phenylosazone, m.p. 122—128°); absence of I leads mainly to a syrup, probably containing ortho-esters. β-*D*-Glucose 1 : 2 : 3 : 4-tetra-acetate (II) with (I) and CaSO<sub>4</sub> in CHCl<sub>3</sub> (presence of I leads mainly to the normal acetate) yields d- (III), m.p. 168—169° (corr.), [α]<sub>D</sub><sup>30</sup> +17.1° in CHCl<sub>3</sub>, and l-(β-*D*-glucoside 1 : 2 : 3 : 4-tetra-acetate)-*D*-mannose 3' : 4' : 6'-triacetate 6 : 1' : 2'-orthoacetate (IV), m.p. 174—174.5° (corr.), [α]<sub>D</sub><sup>32</sup> −27.6° in CHCl<sub>3</sub>, and a residue,



whence very dil. HCl and hot H<sub>2</sub>O yield an amorphous normal octa-acetate (V), softens 83—87°, [α]<sub>D</sub><sup>23</sup> +33.5°. (III) and (IV) are stereoisomerides at C\* of the orthoacetate (A; Ac<sub>4</sub>Gl = glucose tetra-acetate residue linked to C\* by C<sub>(6)</sub>O), since acid removes eight and alkali removes seven Ac. Moreover, in HCl-CHCl<sub>3</sub>, [α]<sub>D</sub><sup>28</sup> of (III) and (IV) changes very rapidly to +44° and +43°, respectively, the rate being independent of the [HCl] provided that 1 mol. of HCl is present; this is followed by a slower decrease in [α], the rate of which is dependent on the [HCl]. In HBr-CHCl<sub>3</sub>, there is a similar very rapid rise in [α], followed by a slower further rise at a rate dependent on the [HBr]. The rapid rises are due to hydrolysis to (II) + acetochloro- or acetobromo-mannose (VI), respectively; this is confirmed by the crude product formed in HBr showing the darkening and evolution of HBr characteristics of (VI). The subsequent slower changes are due to decomp. of (II), which in HCl- or HBr-CHCl<sub>3</sub> shows a decrease and rise, respectively, of [α] at rates similar to those found for (III) and (IV). The normal acetate structure of (V) is shown by removal of 8 Ac by alkali, by stability in HCl-CHCl<sub>3</sub>, and by conversion by HBr-AcOH-Ac<sub>2</sub>O at −2° into acetobromo-6-β-*D*-mannoside-*D*-glucose (VII), m.p. 172—172.5° (rapid heating), decomp. ~182°, [α]<sub>D</sub><sup>30</sup> +151.5° in CHCl<sub>3</sub> [yields two trisaccharides (not yet described)]. With AgOAc-AcOH-I-CaSO<sub>4</sub> in CHCl<sub>3</sub>, (VII) yields an acetate (VIII), softens 90—94°, [α]<sub>D</sub><sup>25</sup> +43°. Purification of (V) or (VIII) by "flowing" chromatography on Al<sub>2</sub>O<sub>3</sub> (freed from alkali by AcOH) yields pure 6-β-*D*-mannosido-β-*D*-glucose octa-acetate (normal form), softens 90—95°, [α]<sub>D</sub><sup>19</sup> +38.9° in CHCl<sub>3</sub>, from which alkali removes eight Ac. R. S. C.

**Synthesis of an epimeric pair of trisaccharides containing mannose units.** E. A. Talley and W. L. Evans (*J. Amer. Chem. Soc.*, 1943, 65, 573—574).—β-*D*-Mannose or -glucose 1 : 2 : 3 : 4-tetra-acetate with acetobromo-6-β-*D*-mannosido-*D*-glucose, CaSO<sub>4</sub>, Ag<sub>2</sub>O, and I in CHCl<sub>3</sub> gives 12-β-*D*-mannosido-epi-β- (I) (46%), m.p. 112—113° (corr.), [α]<sub>D</sub><sup>23</sup> +14.3° in C<sub>6</sub>H<sub>5</sub>N, +11.2° in CHCl<sub>3</sub>, and β-*gentiobiose* hendeca-acetate (58%), m.p. 118—119° (corr.), [α]<sub>D</sub><sup>24</sup> +20.2° in CHCl<sub>3</sub>, respectively, insol. in Et<sub>2</sub>O. The possible identity of (I) with the trisaccharide acetate from "Konjac" mannan (Nishida *et al.*, A., 1930, 1413) is discussed. R. S. C.

**Synthetic glycosides of strophanthidin.** F. C. Uhle and R. C. Elderfield (*J. Org. Chem.*, 1943, 8, 162—169).—Strophanthidin is converted by acetobromoglucose in anhyd. dioxan containing Ag<sub>2</sub>CO<sub>3</sub>, anhyd. MgSO<sub>4</sub>, and I into strophanthidin β-*D*-glucoside tetra-acetate, m.p. 240—250°, softens at ~165° dependent on rate of heating, [α]<sub>D</sub><sup>27</sup> +24° in CHCl<sub>3</sub>. Strophanthidin β-*D*-galactoside tetra-acetate has m.p. 236—237° (decomp.), softens at 230°, [α]<sub>D</sub><sup>28</sup> +16° in CHCl<sub>3</sub>, β-*D*-xyloside triacetate, m.p. 240—250° (decomp.) after softening, [α]<sub>D</sub><sup>28</sup> −10° in CHCl<sub>3</sub>, and β-*L*-arabinoside triacetate, m.p. ~200° (decomp.), softens at ~155° greatly dependent on rate of heating. The acetates are hydrolysed by Ba(OMe)<sub>2</sub> in MeOH to strophanthidin β-*D*-glucoside, m.p. 234—236° (decomp.), softens at 228°, [α]<sub>D</sub><sup>28</sup> +21° in H<sub>2</sub>O, β-*D*-xyloside, m.p. 152—154° (decomp.), [α]<sub>D</sub><sup>25</sup> +7° in 95% EtOH, β-*L*-arabinoside, m.p. ~210° (decomp.) after softening, [α]<sub>D</sub><sup>30</sup> 31° in EtOH, and non-cryst. β-*D*-galactoside. Pharmacologically the glycoside acetates are considerably less potent than the glycosides, which, in turn, are more potent than the aglycons. Introduction of Ac into the latter causes greatly increased activity whereas acetylation of the sugar compound lowers activity in most cases. The activity of the glycosides falls

within the same general range whereas that of their acetates varies over a much wider range.

H. W.

**Constitution of the polysaccharide synthesised by the action of crystalline muscle-phosphorylase.** W. Z. Hassid, G. T. Cory, and R. M. McCready (*J. Biol. Chem.*, 1943, **148**, 89—96).—The *polysaccharide* (I),  $[\alpha]_D^{20} +150^\circ$  in *N*-NaOH, synthesised by the action of cryst. muscle-phosphorylase on glucose 1-phosphate is similar in properties to that formed by potato-phosphorylase and to the amylose fraction from potato starch. It is sparingly sol. in  $H_2O$  and rapidly retrogrades from solution; it produces a more intense blue colour with I than do natural starches and in contrast to the latter is almost completely hydrolysed to maltose by  $\beta$ -amylase. It does not activate muscle-phosphorylase. The methylated synthetic muscle-polysaccharide gives 0.6% of tetramethylglucose on hydrolysis, indicating a chain length of  $\sim 200$  units. The main product of hydrolysis is 2:3:6-trimethylglucose; a small amount of dimethylglucose is also present. (I) appears to consist of long, unbranched chains in which the glucopyranose units are joined by  $\alpha$ -glucosidic linkings between  $C_{(1)}$  and  $C_{(4)}$ .

H. W.

**Solution viscosities of the amylose components of starch.** J. F. Foster and R. M. Hixon (*J. Amer. Chem. Soc.*, 1943, **65**, 618—622).—The dependence of  $\eta$  in  $(CH_2 \cdot NH_2)_2$  on concn. is determined for amylose pptd. from maize, potato, tapioca, and lily bulb starch by BuOH, "cryst." amylose and amyloextrin from maize, amylose extracted from maize by hot  $H_2O$ , and synthetic starch. The results fully confirm the deductions from titration by I (Bates *et al.*, A., 1943, II, 157). Synthetic starch behaves anomalously in both cases, probably owing to heterogeneity.

R. S. C.

**Determination of the liquefaction of starch.** K. Mayer (*Z. physiol. Chem.*, 1939, **262**, 29—36).—The liquefaction of starch by enzyme solutions which contain saccharifying enzymes can be studied by using as substrate starch which has been oxidised by I. This material is not attacked by saccharifying amylases.

H. W.

**Changes of starch during oxidation.** F. F. Farley (*Iowa State Coll. J. Sci.*, 1942, **17**, 57—59; cf. A., 1938, II, 474).—Hydrolysis of maize starch (I) paste oxidised by Br produces 50.7% glycuronic anhydride equiv. and the presence of glycuronic acid units was confirmed by its isolation. Oxime formation is equiv. to a *sec.* OH in 65—75% of the glucose anhydride units.  $CO_2H$  groups are produced in excess of the uronic acid units and there is evidence for splitting of hexose units at a glycol grouping. A mechanical theory of the electrolytic oxidation of (I) granules by alkaline NaOCl is proposed; industrial application of the theory depends on cheap power and the discovery of a suitable anode to replace Pt.

F. R. G.

**Configuration of starch and the starch-iodine complex.** I. Dichroism of flow of starch-iodine solutions. R. E. Rundle and R. R. Baldwin. II. Optical properties of crystalline starch fractions. R. E. Rundle and D. French (*J. Amer. Chem. Soc.*, 1943, **65**, 554—558, 558—561).—I. After staining with I, blue-staining starch pastes and the BuOH-ppt. (I) from maize or potato starch show dichroism of flow (qual. observation described); red-staining starches, waxy maize and glutinous rice starches show only traces of dichroism; glycogen and the residue from (I) purified by adsorption on cellulose show no dichroism. The dichroic solutions absorb light with its electric vector parallel to the flow lines more strongly than if the vector is normal thereto. The dichroism requires that the long axes of the I mols. be parallel to the long axes of the starch-I complex; of two possible structures, one (A) is that in which the starch forms a helix enclosing the I (cf. Freudenberg, A., 1940, II, 120).

II. The cryst. amylose of Kerr *et al.* (A., 1943, II, 156) consists of optically negative, probably uniaxial platelets; after staining with I, these are highly dichroic, light with its electric vector in the plane of the platelets being the more weakly absorbed. The birefringence of (I) is very similar; (I) forms rosettes of flattened spherocrystals and probably consists of the platelets of Kerr *et al.* with the normals in one plane. These results are in best accord with structure (A); a three-dimensional structure is proposed.

R. S. C.

**Oxidation of cellulose; reaction of cellulose with periodic acid.** H. A. Rutherford, F. W. Minor, A. R. Martin, and M. Harris (*J. Res. Nat. Bur. Stand.*, 1942, **29**, 131—141).—In the early stages of the oxidation of cellulose by  $HIO_4$  (when  $\sim 1\%$  of the glucose residues is attacked) the reaction is confined to the oxidation of *sec.* OH groups to CHO and results in the rupture of the C chain between  $C_{(2)}$  and  $C_{(3)}$  of the glucose unit. In accordance with this mechanism 2 CHO result from each mol. of  $HIO_4$  consumed.  $\cdot CHO$  of periodic acid-oxycellulose (I) can be converted into  $\cdot CO_2H$ , titration of which provides an independent check on the content of the former. (I) is characterised by its susceptibility to further attack by alkaline solutions. The alkali-sensitivity of these materials, as measured by solubility in hot, dil. NaOH and by cuprammonium fluidity, appears  $\propto$  CHO content. Alkali-lability practically ceases with the complete transformation of  $\cdot CHO$  into  $\cdot CO_2H$ . This suggests that the sensitivity of (I) to alkali does not depend solely on the rupture of the glucose ring between  $C_{(2)}$  and

$C_{(3)}$  but is related to the sp. instability towards alkali of the dialdehyde formed during the oxidation.

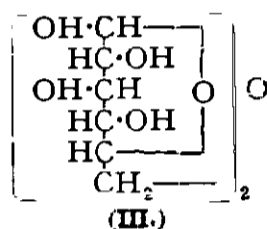
H. W.

**Fractionation of cellulose acetate.** A. M. Sookne, H. A. Rutherford, H. Mark, and M. Harris (*J. Res. Nat. Bur. Stand.*, 1942, **29**, 123—130).—By fractional pptn. by EtOH from  $COMe_2$  solution 2 kg. of technical cellulose acetate has been separated into 15 fractions varying in degree of polymerisation from 30 to 380. The distribution of chain lengths in the initial material (excepting the first fraction) is deduced from the viscosimetrically-determined chain lengths of the fractions. The first fraction is not completely sol. in  $COMe_2$  or  $OH \cdot [CH_2]_2 \cdot OMe$  and therefore no estimate of the degree of polymerisation can be obtained. A large proportion of the ash and haze-producing materials is contained in this first fraction. All the other fractions have very low ash contents and with the exception of the fractions of very low degree of polymerisation the Ac contents are const. A phase diagram showing some of the solubility relationships of the starting material and several of the fractions is given.

H. W.

**Formation of anhydro-structures by alkaline deacylation of a partly substituted cellulose acetate *p*-toluenesulphonate.** T. S. Gardner and C. B. Purves (*J. Amer. Chem. Soc.*, 1943, **65**, 444—449).—A cellulose acetate *p*-toluenesulphonate (A., 1942, II, 397) containing 0.196 primary and 0.054 *sec.*  $p$ - $C_6H_4Me \cdot SO_3$  per glucose residue with an excess of *N*-NaOH in MeOH gives an anhydro-cellulose (I), analysis of which and of the derived  $(Ac_2O \cdot C_6H_5N; 60^\circ)$  acetate (II) suggests presence of 0.060 OMe, 0.007  $p$ - $C_6H_4Me \cdot SO_3$ , and 0.183 anhydro-groups per glucose residue. With 2.3% HCl-MeOH at  $130^\circ$  (40—50 hr.), (II) gives the equilibrium mixture (0.025 mol.) of  $\alpha$ - and  $\beta$ -3:6-anhydroglucofuranoside and an anhydrodihexose (III) (0.022 mol.) [ $Me_8$  derivative (IV), b.p.  $136\text{—}140^\circ/10^{-3}$  mm.,  $[\alpha]_D^{20} +94^\circ$  in  $CHCl_3$ ]. (III) probably has the structure shown, since (IV) is stable to hydrolysis and methanolysis and having regard to the current interpretation of the action of alkali on *p*-toluenesulphonates. Since (I) has a chain-length  $\sim 200$  and swells, but does not dissolve, in 5—17% aq. NaOH, cuprammonium or Triton F solution, or org. solvents, it probably contains many (III) units joined by 1:4- and crossed linkings.

R. S. C.



### III.—HOMOCYCLIC.

**Physical data of monoalkylcyclopentenes and -pentanes.** A. W. Schmidt and A. Gemassmer (*Ber.*, 1940, **73**, [B], 359—366).—Grignard synthesis from  $AlkCl$  and cyclopentanone gives 1-alkyl- $\Delta^1$ -cyclopentenes, hydrogenated ( $PtO_2 \cdot AcOH$ ) to cyclopentanes (cf. A., 1939, II, 361). The following are prepared: 1-octyl-, m.p.  $-36.5^\circ$ , b.p.  $110\text{—}111^\circ/11$  mm., -decyl-, m.p.  $-16.5^\circ$ , b.p.  $111^\circ/0.05$  mm., -dodecyl-, m.p.  $-2.5^\circ$ , b.p.  $117^\circ/0.1$  mm., -tetradecyl-, m.p.  $11.5^\circ$ , b.p.  $128\text{—}130^\circ/0.05$  mm., -hexadecyl-, m.p.  $24.5^\circ$ , b.p.  $148\text{—}150^\circ/0.05$  mm., and -octadecyl- $\Delta^1$ -cyclopentene, m.p.  $30.5^\circ$ , b.p.  $178\text{—}180^\circ/0.05$  mm.; n-octyl-, m.p.  $-44.5^\circ$ , b.p.  $106^\circ/10$  mm., -decyl-, m.p.  $-23.5^\circ$ , b.p.  $117\text{—}118^\circ/0.06$  mm., -dodecyl-, m.p.  $-7.5^\circ$ , b.p.  $116\text{—}117^\circ/0.05$  mm., -tetradecyl-, m.p.  $8^\circ$ , b.p.  $129^\circ/0.05$  mm., -hexadecyl-, m.p.  $19.5^\circ$ , b.p.  $149^\circ/0.05$  mm., and -octadecyl-cyclopentane, m.p.  $28^\circ$ , b.p.  $180^\circ/0.05$  mm. Other physical consts., e.g.,  $d$  and  $\eta$ , are recorded, and some m.p. curves are shown.

A. T. P.

**Production of aromatic hydrocarbons.**—See B., 1943, II, 210.

**Polyisopropylbenzenes. I. Preparation and properties of two di-, two tri-, and one tetra-isopropylbenzene.** A. Newton (*J. Amer. Chem. Soc.*, 1943, **65**, 320—323).—In presence of 96%  $H_2SO_4$  at  $30\text{—}40^\circ$   $C_6H_6$  and  $C_3H_8$  give  $C_6H_4Pr_2$  (1:3-:1:4- 58.6:41.4 pts.),  $C_6H_3Pr_3$  (1:2:4-:1:3:5- 83.7:16.3 pts.),  $C_6H_4Pr_4$  (only 1:2:4:5-), and alkyl sulphates. In presence of  $AlCl_3$  at  $60^\circ$ , there are formed  $C_6H_4Pr_2$  (1:3-:1:4- 65.4:34.6 pts.),  $C_6H_3Pr_3$  (only 1:3:5-), and  $C_6H_2Pr_4$  (only 1:2:4:5-). Physical properties of the products are given.

R. S. C.

**Rearrangements in the Friedel-Crafts alkylation of benzene.** H. Gilman and R. N. Meals (*J. Org. Chem.*, 1943, **8**, 126—146).—Examination of the literature shows that primary alkyl compounds give both primary and *sec.*-alkylbenzenes and higher temp. favour the formation of the latter. *sec.*-Alkyl compounds afford *sec.* and never primary alkylbenzenes. *iso*-Alkyl compounds appear to have little tendency to form *iso*-alkylbenzenes and give largely *tert.*-alkylbenzenes which are the exclusive products from *tert.*-alkyl compounds. Under mild experimental conditions  $C_6H_6$  and a primary *n*-alkyl bromide in presence of  $AlCl_3$  give a mixture of alkylbenzenes in which Ph is probably attached to each C of the alkyl residue. The evidence obtained does not indicate any appreciable branching of the alkyl chain under the experimental conditions used.  $n$ - $C_6H_{13}Br$  and  $C_6H_6$  in presence of  $AlCl_3$  give  $\alpha$ -,  $\beta$ -, and  $\gamma$ -phenylhexane and  $n$ - $C_{12}H_{25}Br$  affords a mixture of dodecylbenzenes in which  $\alpha$ - and  $\zeta$ -phenyldodecane have been identified. The  $\alpha$ -Ph derivatives have been isolated from  $C_6H_6$  and  $n$ - $C_{14}H_{29}Br$ ,  $n$ - $C_{16}H_{33}Br$ , and  $n$ - $C_{18}H_{37}Br$ . The  $\alpha$ -phenylalkanes are prepared

synthetically by Clemmensen reduction of the appropriate Ph alkyl ketone or by the Wurtz-Fittig reaction. *sec.*-Alkylbenzenes are obtained from the appropriate ketone and Grignard reagent followed by dehydration of the carbinol with 60%  $\text{H}_2\text{SO}_4$  and subsequent reduction of the olefine by Na and EtOH. The hydrocarbons are finally transformed into their sulphonamides or derivatives thereof. The following are described: *n*-hexadecyl-, b.p. 202—213°/7 mm., *n*-tetradecyl-, b.p. 188—189°/6 mm., *n*-dodecyl-, b.p. 164°/4 mm., *n*-heptyl-, b.p. 240—244°/1 atm., and *n*-hexyl-benzene, b.p. 220—222°/1 atm.;  $\beta$ -phenyldodecan- $\beta$ -ol, b.p. 174—177°/7 mm.;  $\gamma$ -phenyldodecan- $\gamma$ -ol, b.p. 168°/5 mm.;  $\gamma$ -phenyldodecan- $\delta$ -ol, b.p. 170°/4 mm.,  $\epsilon$ -phenyldodecan- $\epsilon$ -ol, b.p. 166—168°/5 mm.,  $\zeta$ -phenyldodecan- $\zeta$ -ol, b.p. 169—170°/6 mm.,  $\beta$ -phenylhexan- $\beta$ -ol, b.p. 120°/10 mm., and  $\gamma$ -phenylhexan- $\gamma$ -ol, b.p. 134°/27 mm.,  $\beta$ -, b.p. 160—162°/5 mm.,  $\gamma$ -, b.p. 165°/7 mm.,  $\delta$ -, b.p. 153—154°/5 mm.,  $\epsilon$ -, b.p. 156—157°/6 mm., and  $\zeta$ -, b.p. 161°/9 mm., -phenyldodecene,  $\beta$ -, b.p. 125—130°/42 mm., and  $\gamma$ -, b.p. 125—130°/56 mm., -phenylhexene;  $\beta$ -, b.p. 161°/7 mm.,  $\gamma$ -, b.p. 171°/13 mm.,  $\delta$ -, b.p. 164°/17 mm.,  $\epsilon$ -, b.p. 158°/7.5 mm., and  $\zeta$ -, b.p. 153°/6 mm., -phenyldodecane,  $\beta$ -, b.p. 208.7—210°/741 mm., and  $\gamma$ -, b.p. 200—203.5°/1 atm., -phenylhexane; hexadecyl-, m.p. 97°, tetradecyl-, m.p. 97.5—98°, dodecyl-, m.p. 97.5°,  $\alpha$ -methylundecyl-, m.p. 99°,  $\alpha$ -ethyldecyl-, m.p. 56°,  $\alpha$ -*n*-propylundecyl-, m.p. 60°, heptyl-, m.p. 90.5°, hexyl-, m.p. 86°, and  $\alpha$ -methylamyl-, m.p. 83°, -benzenesulphonamides;  $\alpha$ -ethyldecyl-, m.p. 103°,  $\alpha$ -*n*-propylundecyl-, m.p. 112—112.5°,  $\alpha$ -*n*-butyldecyl-, m.p. 107—107.5°, and  $\alpha$ -*n*-amylheptyl-, m.p. 128°, - $\beta$ -naphthalenesulphonamides; acetamido-derivatives, m.p. 91°, 76°, and 127°, respectively, of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -hexylbenzene and corresponding diacetamido-compounds, m.p. 200—202°, 178°, and 199—201°, respectively.

H. W.

**Polymerisation of styrene in presence of 3 : 4 : 5-tribromobenzoyl peroxide.** C. C. Price and B. E. Tate (*J. Amer. Chem. Soc.*, 1943, 65, 517—520).—3 : 4 : 5- $\text{I-C}_6\text{H}_3\text{Br}_3\text{-CO}_2\text{H}$  [best (60%) prepared from  $p\text{-NH}_2\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$  according to Sudborough (A., 1894, i, 244)] with  $\text{SOCl}_2$  and then  $\text{Na}_2\text{O}_2\text{-C}_6\text{H}_6$  at 0.5° gives *di*-3 : 4 : 5-tribromobenzoyl peroxide (I) (18%), m.p. 183—185°. With (I) in  $\text{C}_6\text{H}_6$  or dioxan,  $\text{CH}_2\text{:CHPh}$  (II) gives polymers,  $\text{C}_6\text{H}_2\text{Br}_3(\text{C}_6\text{H}_5)_{12}\text{O}_3$ ,  $\text{C}_6\text{H}_2\text{Br}_3(\text{C}_6\text{H}_5)_{15}\text{O}_7$ , and  $\text{C}_6\text{H}_2\text{Br}_3(\text{C}_6\text{H}_5)_{36}\text{O}_{18}$ . Presence of one  $\text{C}_6\text{H}_2\text{Br}_3$  per mol. indicates the reaction mechanism, but the source of the O is unknown. Very little Br is introduced into polystyrene (III) by (I) in  $\text{C}_6\text{H}_6$ .  $k$  for removal of (I) from  $\text{C}_6\text{H}_6$  at 80° in presence of (II) is 0.0102—0.0108, but in presence of (III) is 0.0019.  $\text{Bz}_2\text{O}_2$  and (II) in dioxan give a polymer,  $\text{Ph}(\text{C}_6\text{H}_5)_{31}\text{O}_3$ , only slightly degraded by boiling conc.  $\text{HCl-AcOH}$ . O-free (III) is unaffected by peroxide-containing dioxan in light.

R. S. C.

**Ester groups in polystyrene made with chloro- and bromo-benzoyl peroxides.** P. D. Bartlett and S. G. Cohen (*J. Amer. Chem. Soc.*, 1943, 65, 543—546).—Styrene and ( $p\text{-C}_6\text{H}_4\text{Br-CO}_2$ )<sub>2</sub> (I) (explodes at 148°) in boiling  $\text{C}_6\text{H}_6$  give polymers containing 10.7% (II) and 11.5% of Br. (II) is stable to boiling 20% aq. KOH (cf. Price *et al.*, A., 1942, II, 304), but, when boiled for a long time with  $\text{NaOEt-EtOH}$ , yields 53% of  $p\text{-C}_6\text{H}_4\text{Br-CO}_2\text{H}$  and a residue containing 36% of the Br. Thus, (II) contains ~36% of the (I) as  $p\text{-C}_6\text{H}_4\text{Br}$  and ~64% as  $p\text{-C}_6\text{H}_4\text{Br-CO}_2$ . Hydrolysis of (II) by  $\text{NaOEt-EtOH-PhMe}$  with later addition of  $\text{H}_2\text{O}$  is less satisfactory. Styrene and ( $p\text{-C}_6\text{H}_4\text{Cl-CO}_2$ )<sub>2</sub> (decomp. 138°) at 81—84° and then 100—103° give a polymer containing 0.096% of Cl, which by hydrolysis by  $\text{NaOEt-EtOH-PhMe}$  with later addition of  $\text{H}_2\text{O}$  is shown to contain ~12% of  $p\text{-C}_6\text{H}_4\text{Cl}$ , but the Cl content (0.015%) of the monomer renders this result uncertain.

R. S. C.

**Addition of triphenylmethyl to  $\beta$ -methyl- $\Delta^a$ -buten- $\gamma$ -inene.** A. F. Thompson, jun., and D. M. Surgenor (*J. Amer. Chem. Soc.*, 1943, 65, 486—487).— $\text{CPh}_3\text{Cl}$ , Hg, and  $\text{CH}_2\text{:CMe:CH}_2$  in  $\text{C}_6\text{H}_6\text{-N}_2$  at room temp. give *aaayyy-hexaphenyl- $\delta$ -methyl- $\Delta^{\beta\gamma}$ -hexadiene* (47%), m.p. 184—185.5° [contains 2 C:C ( $\text{H}_2\text{-PtO}_2\text{-AcOH}$ )], which with  $\text{O}_3$  in  $\text{EtOAc}$  at 0°, then  $\text{H}_2\text{-Pd-CaCO}_3$ , and finally  $\text{Ag}_2\text{O}$  gives  $\text{CPh}_3\text{-CO}_2\text{H}$  and  $\text{COMe-CH}_2\text{-CPh}_3$ .

R. S. C.

**Dialkylation of naphthalene. II. Synthesis of 2 : 6-diphenylnaphthalene.** C. C. Price and A. J. Tomisek (*J. Amer. Chem. Soc.*, 1943, 65, 439—440; cf. A., 1943, II, 126).—Phenylsuccinic anhydride (prep. from the acid by  $\text{AcCl}$ ),  $\text{Ph}_2$ , and  $\text{AlCl}_3$  in boiling  $\text{CS}_2$  give 4- $\beta$ -carboxy- $\alpha$ -phenylpropionylphenyl, m.p. 175.5—176°, oxidised by  $\text{KMnO}_4$  to  $p\text{-C}_6\text{H}_4\text{Ph-CO}_2\text{H}$  and reduced by  $\text{Zn-Hg-conc. HCl-AcOH-C}_6\text{H}_6$  to  $\beta$ -phenyl- $\gamma$ -4-diphenylbutyric acid, m.p. 120.5—121°, which with, successively,  $\text{SOCl}_2$ ,  $\text{AlCl}_3\text{-CS}_2$ ,  $\text{Zn-Hg-HCl-AcOH-C}_6\text{H}_6$ , and Se at 290—320° gives 2 : 6- $\text{C}_{10}\text{H}_6\text{Ph}_2$ , m.p. 233—234°, thus proving the structures of the products of Boudroux (A., 1929, 1050) and Pokrovskaja *et al.* (A., 1940, II, 161).

R. S. C.

**Electronic distribution and chemical reactivity in condensed unsaturated hydrocarbons.** N. Svartholm (*Arkiv Kemi., Min., Geol.*, 1942, 15, A, No. 13, 13 pp.).—A discussion of the  $\text{C}_{10}\text{H}_8$  mol. indicates that a picture of the electron distribution can be obtained by a comparison of separate superposition diagrams for unexcited and singly excited structures. This method is applied to anthracene, phenanthrene, chrysene, 1 : 2-benzanthracene (I), pyrene, 1 : 2 : 3 : 4- and 1 : 2 : 5 : 6-dibenzanthracene, and 3 : 4-benzpyrene. A closer

quantum-mechanical study of electron distribution in (I) gives a superposition diagram in general agreement with the simpler treatment. Electron distributions in (I) and the three last-named compounds are briefly correlated with chemical reactivity.

A. J. E. W.

**Action of magnesium methyl iodide on methyl  $\alpha$ -phenylcinnamate. Synthesis of 2-phenyl-1 : 1-dimethylindene.** C. F. Koelsch and P. R. Johnson (*J. Amer. Chem. Soc.*, 1943, 65, 565—567).— $\text{CHPh:CPh-CO}_2\text{H}$  (I) (from  $\text{CH}_2\text{Ph-CO}_2\text{H}$ ,  $\text{PhCHO}$ , and  $\text{NaOAc}$  in  $\text{Ac}_2\text{O}$ ) with  $\text{MeOH-H}_2\text{SO}_4$  gives the Me ester, which with  $\text{MgMeI}$  in  $\text{Et}_2\text{O}$  gives  $\text{CHPh:CPh-CMe}_2\text{-OH}$  (II) (50%), m.p. 69—70° (lit. 68°) (absorbs Br; gives no  $\text{CHI}_3$ ).  $\text{Ph-[CH}_2\text{:C-CO}_2\text{H}$  [obtained (85%) by electrolytic reduction of (I)] gives the Me ester, b.p. 168°/8 mm., which with  $\text{MgMeI-Et}_2\text{O}$  yields  $\gamma\delta$ -diphenyl- $\beta$ -methylbutan- $\beta$ -ol (86—88%), m.p. 68—69°, dehydrated by  $\text{H}_2\text{SO}_4\text{-AcOH}$  at 100° to  $\alpha\beta$ -diphenyl- $\gamma$ -methyl- $\Delta^{\beta}$ -*n*-butene (III), b.p. 150°/10 mm. Oxidation of (III) by  $\text{CrO}_3\text{-AcOH}$  at room temp. gives  $\text{CH}_2\text{Ph-COPh}$ , but Br in  $\text{CHCl}_3$ , later boiling  $\text{AcOH}$ , gives 2-phenyl-1 : 1-dimethylindene (IV) (45%), m.p. 61—62°, also obtained in ~10% yield from (II) by  $\text{H}_2\text{SO}_4\text{-AcOH}$  and oxidised by  $\text{CrO}_3\text{-AcOH}$  to  $\alpha$ -o-carboxyphenylisobutyrophenone (V), m.p. 210—211° (stable to  $\text{KMnO}_4$ ). The products of Earl *et al.* (A., 1931, 340) formulated as (IV) and (V) are 3-phenyl-1 : 1-dimethylindene and  $\alpha$ -o-benzoylphenylisobutyric acid, respectively.

R. S. C.

**Thermal isomerisation of indene derivatives.** C. F. Koelsch and P. R. Johnson (*J. Amer. Chem. Soc.*, 1943, 65, 567—573).—Pyrolysis of 1 : 3- (I), 1 : 2- (II), or 2 : 3-diphenylindene (III) at 450° in  $\text{N}_2$  gives an equilibrium mixture, (I) 8—20%, (II) 4—6%, (III) 47—65%, which is unchanged by further pyrolysis (cf. A., 1940, II, 355). The still readier isomerisation, (II)  $\rightleftharpoons$  (III), prevents deduction whether the Ph migrates from  $\text{C}_{(3)}$  or  $\text{C}_{(1)}$ . The possibility of migration from  $\text{C}_{(1)}$  is proved by three examples. (i) At 490° 1 : 1 : 3-triphenylindene [prepared by interaction of  $\text{CPh}_2\text{:CH-MgBr}$  with  $\text{COPh}_2$  to give  $\text{CPh}_2\text{:CH-CPh}_2\text{-OH}$  (in  $\text{AcOH}$  gives  $\text{CPh}_2\text{:C:CPh}_2$ ) and subsequent dehydration by  $\text{H}_2\text{SO}_4\text{-AcOH}$ ; 64% yield] gives 86% of 1 : 2 : 3-triphenylindene (and a red gum), which is also obtained from 2 : 3-diphenylindene by  $\text{MgPhBr}$ , followed by  $\text{AcOH} + \text{H}_2\text{SO}_4$  (1 drop). (ii) Rapid pyrolysis of 3'-phenylspirofluorene-9 : 1'-indene (IV) at 490° gives, probably reversibly, 80% of 9-phenyl-1 : 2 : 3 : 4-dibenzfluorene and 17% of unchanged (IV). (iii) 1 : 3-Diphenyl-1-methylindene (prep. from 3-phenyl-3-methylindan-1-one by  $\text{MgPhBr}$  and then  $\text{H}_2\text{SO}_4\text{-AcOH}$ ), m.p. 59—60°, at 470° gives irreversibly 82% of a mixture of 2 : 3-diphenyl-1- (V), m.p. 106.5°, and 1 : 2-diphenyl-3-methylindene (VI), m.p. 91°, and an oil which with  $\text{CrO}_3\text{-AcOH}$  yields  $o\text{-C}_6\text{H}_4\text{Bz}_2$ ,  $o\text{-C}_6\text{H}_4\text{Bz-CO}_2\text{H}$  (VII), and  $\text{BzOH}$ ; the (VII) is derived from 1 : 3-diphenyl-3-methylindene, formed to a small extent by migration of Me. Structures are proved as follows. Crude  $\text{CHMeBr-CHBr-CO}_2\text{H}$  (prep. from  $\text{CHMe:CH-CO}_2\text{H}$  and Br in  $\text{Et}_2\text{O}$  at 10—15°) with  $\text{C}_6\text{H}_6$  and  $\text{AlCl}_3$  gives  $\text{CHPhMe-CHPh-CO}_2\text{H}$ , m.p. 182—183° (lit. 180—181°), which with hot  $\text{PCl}_5$  and then  $\text{AlCl}_3\text{-C}_6\text{H}_6$  gives 2-phenyl-3-methylindanone (70%), m.p. 84.5—86°, b.p. 196—200°/13 mm.; with  $\text{MgPhBr}$  and then 1%  $\text{H}_2\text{SO}_4\text{-AcOH}$  this gives 79% of (V). 2 : 3-Diphenylindanone similarly yields 70% of (VI). Me migrates only if the ring contains also Ph. 3-Methylindone, b.p. 91—92°/24 mm. [ $\text{OMe-C}_6\text{H}_4\text{:CH}$  derivative, m.p. 114—115° (lit. 113°); picrate, m.p. 76—77°], in 1%  $\text{H}_2\text{SO}_4\text{-AcOH}$  at room temp. yields a non-volatile, oily polymeride, depolymerised by distillation with a few drops of  $\text{H}_2\text{SO}_4$  at 1 atm., but is unchanged by pyrolysis at 490° (cf. Mayer *et al.*, A., 1921, i, 554). 2-Hydrindone and  $\text{MgMeI}$  give 2-methylindan-2-ol (VIII) (73%), m.p. 52—53° (lit. 52°), anhydrous-2-hydrindone (IX), m.p. 173—176°, and a product, m.p. 156—157°, probably obtained from (IX) and  $\text{MgMeI}$ ; dehydration of (VIII) in boiling  $\text{C}_6\text{H}_6$  by  $\text{P}_2\text{O}_5$  ( $\text{H}_2\text{SO}_4\text{-AcOH}$  gives a polymeride) gives 2-methylindene (55%), b.p. 97—99°/24 mm. (unstable picrate, m.p. 79—79.5°), unchanged by pyrolysis at 490°. At 490° 3-phenyl-1 : 1-dimethylindene (X), m.p. 50—51°, b.p. 184—187°/27 mm. [(? 2- $\text{NO}_2$ -derivative, m.p. 141—142°], gives ~63% of unchanged (X) and 26% of 3-phenyl-1 : 2- (XI) + 1-phenyl-2 : 3-dimethylindene (XII), since the oily mixture with  $\text{CrO}_3\text{-AcOH}$  at room temp. yields  $o\text{-C}_6\text{H}_4\text{Bz-CMe}_2\text{-CO}_2\text{H}$  (XIII) and 2-acetylbenzophenone (XIV), m.p. 99° [disemicarbazone, m.p. 214—216° (decomp.)], whereas (X) gives only (XIII) and (XII) gives only (XIV). Pyrolysis of (XII) also gives (X), (XI), and (XII). 60% of unchanged 2-phenyl-1 : 1-dimethylindene is recovered after pyrolysis at 490°, but the oily fraction yields  $o\text{-C}_6\text{H}_4\text{Bz-CO}_2\text{H}$  (indicating migration of Ph from  $\text{C}_{(2)}$ ), and possibly (XIII), which would arise from (X). Migration from  $\text{C}_{(2)}$  thus occurs if  $\text{C}_{(1)}$  is fully substituted, but a secondary rearrangement then occurs. A mobile H on the indene is essential for the migration. The reaction mechanisms are discussed.

R. S. C.

**Resonance structure of anthracene and phenanthrene.** C. V. Jonsson (*Arkiv Kemi., Min., Geol.*, 1942, 15, A, No. 14, 9 pp.).—The electron distributions, bond strengths, and resonance energies ( $R$ ) in  $\text{C}_{10}\text{H}_8$ , anthracene (I), and phenanthrene (II) are considered. A simplified quantum-mechanical treatment is employed in which only unexcited and singly excited canonical structures are included; the no. of structures to be considered is thus reduced to 52 for (I)

or (II). For (I) and (II), respectively,  $R = 4.54$  and  $4.78$  e.v., and vals. of the exchange integral (which are probably several % too high) are 1.60 and 1.63. The relative strength of a linking can be estimated by counting the no. of possible unexcited structures in which it occurs. A less reliable estimate of the probable electron density at a given atom may be made by counting the no. of singly excited structures in which ineffective linkings start from that atom.

A. J. E. W.

**Dehydrogenation.** VII. S. C. Sen-Gupta (*J. Indian Chem. Soc.*, 1942, 19, 467—472).—With  $C_6H_6$  ( $AlCl_3$ ), the anhydride of 1-carboxycyclohexyl-1-acetic acid (at room temp., then at 60—65°) [or the acid chloride of Me 1-carboxycyclohexyl-1-acetate (at room temp.)] yields 1-phenacyl- (I), m.p. 117—118° (semicarbazone, m.p. 132—133°), [or its Me ester, b.p. 165—170°/3 mm., m.p. 65—66°], reduced (Clemmensen) to 1- $\beta$ -phenylethyl-cyclohexane-1-carboxylic acid, m.p. 93° (Et ester, b.p. 111—112°/5 mm.; anilide, m.p. 130—131°), cyclised by 75% (vol.)  $H_2SO_4$  to 1-keto-, b.p. 145°/3 mm. (semicarbazone, m.p. 187—188°), which on Clemmensen reduction yields 1:2:3:4-tetrahydronaphthalene-2:2-spirocyclohexane, b.p. 115—117°/3 mm. Se-dehydrogenation of this yields phenanthrene. 1-p-Methylphenacyl- (prep. as above), m.p. 129—130° (semicarbazone, m.p. 166°; Me ester, b.p. 180—182°/5 mm., m.p. 65—66°), similarly yields 1- $\beta$ -p-tolylethyl-cyclohexane-1-carboxylic acid, m.p. 99—100° (Et ester, b.p. 115—116°/6 mm.; p-toluidide, m.p. 128—129°), and 1-keto-7-methyl-, b.p. 158—160°/4 mm. (oxime, m.p. 139—140°), and 7-methyl-1:2:3:4-tetrahydronaphthalene-2:2-spirocyclohexane, b.p. 155—156°/8 mm., dehydrogenated to 3-methylphenanthrene, whilst 1-p-ethylphenacyl-, m.p. 117—118° (semicarbazone, m.p. 144°; Me ester, b.p. 202—203°/7 mm.), gives 1- $\beta$ -p-ethylphenylethyl-cyclohexane-1-carboxylic acid, m.p. 87—88° (Et ester, b.p. 104—105°/6 mm.), and 1-keto-7-ethyl-, b.p. 195—197°/9 mm. (semicarbazone, m.p. 203—204°), and 7-ethyl-1:2:3:4-tetrahydronaphthalene-2:2-spirocyclohexane, b.p. 168—169°/8 mm., dehydrogenated to 3-ethylphenanthrene. In no case was any anthracene derivative obtained.

A. Li.

**Aromatic cyclodehydration.** X. 10-Phenyl-9-alkyl- or -9-aryl-anthracenes. C. K. Bradsher and E. S. Smith (*J. Amer. Chem. Soc.*, 1943, 65, 451—452; cf. A., 1941, II, 127).—Crude  $o$ - $C_6H_4Cl$ - $CHPh_2$ ·OH with red P and I in boiling AcOH gives  $o$ - $C_6H_4Cl$ - $CHPh_2$  (47.5%), converted by  $CuCN$  in  $C_6H_5N$  at 200° into  $o$ - $CN$ - $C_6H_4$ - $CHPh_2$  (I) (81%), m.p. 82—84° (lit. 89°). With  $MgPhBr$ , (I) gives an imine, hydrolysed only by boiling  $HCl$  to  $o$ - $C_6H_4$ - $Bz$ - $CHPh_2$  (60%), m.p. 84—86°, which in boiling 34% aq.  $HBr$ - $AcOH$  (81% yield) or with 2 drops of  $H_2SO_4$  in  $AcOH$  at 100° (95% yield) gives 9:10-diphenylanthracene, m.p. 247—248°. With  $MgRI$ , (I) gives similarly 9-phenyl-10-methyl- (50%), m.p. 112.5—113.5°, and -10-ethyl-anthracene (47.5%), m.p. 107—108.5°.

R. S. C.

**Condensation of unsaturated amines with aromatic compounds.** Preparation of  $\beta$ -substituted phenylethylamines. A. W. Weston, A. W. Ruddy, and C. M. Suter (*J. Amer. Chem. Soc.*, 1943, 65, 674—677).—In presence of  $AlCl_3$  (3 mols.), but not of  $BF_3$ - $Et_2O$  or conc.  $H_2SO_4$ , at 0° and later the b.p.,  $CH_2$ : $CH$ : $CH_2$ : $NH_2$  (1 mol.) and  $C_6H_6$  (excess) give 85—94% of  $CHPhMe$ : $CH_2$ : $NH_2$  (I), b.p. 97—98°/19 mm. [m.p. 143—144.5° (lit. 146—147°, 123—124°); this and other m.p. in parentheses refer to the hydrochlorides].  $PhF$  and  $PhMe$  give similarly mainly  $\beta$ -p-fluorophenyl- (59%), b.p. 105—106°/22 mm. (m.p. 149—150°), and  $\beta$ -p-tolyl-n-propylamine (90%), b.p. 116—117°/22 mm. (m.p. 174—176°), respectively, orientations being proved by oxidation to impure  $p$ - $C_6H_4F$ : $CO_2H$  and  $p$ - $C_6H_4$ : $(CO_2H)_2$ , respectively. Condensation with  $PhOMe$  was unsuccessful.  $p$ - $C_6H_4Me$ : $SO_2$ : $NMe$ : $CH_2$ : $CH$ : $CH_2$  [prep. from  $p$ - $C_6H_4Me$ : $SO_2$ : $NHMe$  by  $CH_2$ : $CH$ : $CH_2Cl$  (II) and  $KOH$  in a little  $EtOH$ ; 89% yield], b.p. 190—193°/12 mm., and  $Na$  in  $Bu^oOH$  give 48% of  $CH_2$ : $CH$ : $CH_2$ : $NHMe$ , b.p. 65°. 33%  $NH_2Et$  and (II) give  $CH_2$ : $CH$ : $CH_2$ : $NH_2$  (43%), b.p. 82—84°, and ethyldiallylamine, b.p. 129—130°.  $CH_2$ : $CH$ : $CH_2$ : $NMe_2$ , b.p. 61—64°, is obtained (~30%) by shaking  $NHMe_2$ : $HCl$  with (II) and aq.  $NaOH$  at >1 atm. 33%  $NH_2Me$  and  $CH_2$ : $CH$ : $CH_2Cl$  in warm  $EtOH$  give methyl-di- $\beta$ -methylallylamine (78%), b.p. 145—145.5°, and methyl- $\beta$ -methylallylamine (15%), b.p. 86—86.5°;  $NHMe_2$  gives dimethyl- $\beta$ -methylallylamine (41%), b.p. 82.4—82.6°/750 mm. The appropriate substituted allylamine with  $C_6H_6$  and  $AlCl_3$  gives  $\beta$ -phenyl-n-propyl-methyl- (III) (47%), b.p. 86—87°/10 mm. [m.p. 145—145.5° (lit. 148—159°)], -ethyl- (77%), b.p. 93°/10 mm. (m.p. 158.5—159.5°), -n-butyl- (66%), b.p. 121—123°/12 mm. (m.p. 154—155.5°), -dimethyl- (62%), b.p. 79—80°/10 mm. (m.p. 221—222.5°), and -di-n-butyl-amine (45%), b.p. 148—150°/12 mm., and  $\beta$ -phenyl-isobutyl-amine (84%), b.p. 75—76°/5 mm. (m.p. 200—201.5°), -methylamine (70%), b.p. 84—85°/9 mm. (m.p. 218.5—219.5°), and -dimethylamine (83%), b.p. 87—88°/10 mm. (m.p. 199—200°).  $CHPhMe$ : $CH_2Br$  with  $NH_3$ - $EtOH$  at 80—90° gives 32% of (I) and much  $CH_2$ : $CHPhMe$  (IV), and with  $NH_2Me$ - $EtOH$  at 5° gives 32% of (III) and 51% of (IV). The oral toxicity of most of the hydrochlorides to mice is recorded.

R. S. C.

**N-Benzylamides as derivatives for identifying the acyl groups in esters.**—See A., 1943, II, 248.

**Derivatives of 1:2:4:5-tetrachlorobenzene.** I. Nitro- and amino-compounds. A. T. Peters, F. M. Rowe, and D. M. Stead (*J. C.S.*, 1943, 233—235).—2:3:5:6:1- $C_6HCl_4$ : $NH_2$  (I), m.p. 107—108° (lit. 90°) (improved prep.) (diazonium zincchloride; azo- $\beta$ -naphthol, m.p. 212°;  $Ac_1$ , m.p. 213—214°, and  $Ac_2$  derivative, m.p. 175—176°), is diazotised by  $NO$ : $SO_4H$  at 60°. With 2:3- $OH$ : $C_{10}H_7$ : $COCl$ : $PhNO_2$ , (I) affords 2:3:5:6-tetrachloro-2'-hydroxy-3'-naphthanilide, m.p. 232°. Diazotised (I) with aq.  $NaOAc$  at room temp. (4 days) yields 3:4:6-trichlorobenzene-2-diazo-1-oxide, m.p. 117—118° (decomp.). 2:3:5:6:1:4- $C_6Cl_4(NO_2)_2$  (II) (modified prep.) and  $Sn$ - $HCl$ - $EtOH$  or  $Na_2S_2O_4$ -aq.  $EtOH$  give the corresponding diamine, m.p. 222—223° [ $Ac_1$  (III), m.p. 276°, and  $Ac_2$  derivative, m.p. 205—209°]. Diazotisation ( $NO$ : $SO_4H$ ) of (III) followed by coupling, gives 2:3:5:6-tetrachloro-4-aminobenzeneazo- $\beta$ -naphthol, m.p. 257—258° (decomp.). (II) with aq.  $Na_2S_2O_4$ - $EtOH$ , or 2.8N- $EtOH$ - $NH_3$  at 110—120°, yields 2:3:5:6-tetrachloro-4-nitroaniline, m.p. 216—217° [ $AcCl$ - $PhMe$  at 110—120° gives the  $Ac_1$ , m.p. 252—253°, and boiling  $Ac_2O$ - $H_2SO_4$  yields the  $Ac_2$  derivative, m.p. 168—169°, reduced by  $Na_2S_2O_4$ -aq.  $EtOH$  to 2:3:5:6-tetrachloro-4-aminodiacetanilide, m.p. 194—195°]; diazotisation ( $NO$ : $SO_4H$  at 60°) and coupling then gives the azo- $\beta$ -naphthol, m.p. 282—284° (decomp.), and the azo-2'-hydroxy-3'-naphthanilide, m.p. 296° (decomp.). 2:3:5:6-Tetrachloro-4-nitro-2'-hydroxy-3'-naphthanilide has m.p. 269—270°. 4:2:3:5:6:1- $NO_2$ : $C_6Cl_4$ : $OMe$  (IV), m.p. 112—113° (lit. 105—106°), prepared from 2:3:5:6:1- $C_6HCl_4$ : $OMe$  and  $HNO_3$  (d 1.5) at 0°, or from (II) and 0.2N- $NaOMe$ , is reduced by  $Na_2S_2O_4$ -aq.  $EtOH$  to the corresponding amine (V), m.p. 107—108° ( $Ac_2$  derivative, new m.p. 105—106°; azo- $\beta$ -naphthol, m.p. 204—205°; 2:3:5:6-tetrachloro-4-methoxy-2'-hydroxy-3'-naphthanilide, m.p. 208°). 2:3:5:6:1- $C_6HCl_4$ : $OH$  and  $HNO_3$  (d 1.5)- $AcOH$  at 10° give 2:3:5:6-tetrachloro-4-nitrophenol, m.p. 148—149° (decomp.) (acetate, m.p. 113—114°), also obtained in small yield during amination of (II), and in the prep. of (IV) by  $NaOMe$ . Diazotised (V) with aq.  $NaOAc$  at room temp. yields 2:3:5:6-tetrachlorobenzene-4-diazo-1-oxide, explodes at 131° (darkens at 120°), converted by  $Ac_2O$  into 2:3:5:6:1:4- $C_6Cl_4(OAc)_2$ , and by  $\beta$ - $C_{10}H_7$ : $OH$  in 1%  $NaOH$  into 2:3:5:6-tetrachloro-4-hydroxybenzeneazo- $\beta$ -naphthol, m.p. 264—265° (decomp.), also obtained from the diazo-oxide derived from 4:2:3:5:6:1- $NO_2$ : $C_6Cl_4$ : $N_2HSO_4$  (replacement of  $NO_2$ ).

A. T. P.

**Ethyl p-aminobenzenesulphonate.** L. A. Walter (*J. Amer. Chem. Soc.*, 1943, 65, 739).—Et sulphanilate, m.p. 78—80°, unstable, is prepared by hydrogenating ( $PtO_2$ ; 30—40 lb.;  $HCl$ - $EtOH$ )  $p$ - $NO_2$ : $C_6H_4$ : $SO_3Et$  and is isolated as unstable hydrochloride.

R. S. C.

**Derivatives of 2:5-diaminobenzenesulphonamide.** A. R. Goldfarb and B. Berk (*J. Amer. Chem. Soc.*, 1943, 65, 738—739).—5:2:1- $NO_2$ : $C_6H_3Cl$ : $SO_2Cl$  (I) (from  $p$ - $C_6H_4Cl$ : $NO_2$  and  $ClSO_3H$  at 120—130°), m.p. 85—87°, with 28% aq.  $NH_3$  gives the amide (II), m.p. 184—185°, which with  $CuSO_4$ -( $NH_4$ ) $_2$  $CO_3$ -28% aq.  $NH_3$  at 120° gives 5:2:1- $NO_2$ : $C_6H_3(NH_2)_2$ : $SO_2$ : $NH_2$  (86%), m.p. 208°, reduced (alkaline  $Na_2S_2O_4$ ) to 2:5:1-( $NH_2$ ) $_2$ : $C_6H_3$ : $SO_2$ : $NH_2$  (70%), m.p. 184°. With  $CaCO_3$ - $CO_2$  in boiling  $NH_4Ph$ , (II) gives 5:2:1- $NO_2$ : $C_6H_3(NHPh)$ : $SO_2$ : $NH_2$ , m.p. 168—169°, and thence ( $Na_2S_2O_4$  or  $H_2$ -Raney  $Ni$ - $EtOH$ ) 5-amino-2-anilinobenzenesulphonamide, m.p. 164°.  $OH$ :[ $CH_2$ ] $_2$ : $NH_2$  (excess), (I), and  $KOH$  in  $H_2O$  give, with cooling, 2-chloro-5-nitro- (58%), m.p. 133—135°, or, without cooling, 5-nitro-2- $\beta$ -hydroxyethylamino- (73%), m.p. 119—120°, converted as above into 5-nitro-2-amino-, m.p. 149—150°, 2:5-diamino- (dihydrochloride, m.p. 184°), and 5-amino-2- $\beta$ -hydroxyethylamino-, m.p. 162—163°, -benzenesulphon- $\beta$ -hydroxyethylamide.

R. S. C.

**Alkylphenols.**—See B., 1943, II, 210.

**o- and m-Tolyl butyrate.** Preparation and properties. B. E. Mirza and G. D. Advani (*J. Univ. Bombay*, 1943, 11, A, Part 5, 87—91).—o- and m-Cresol with  $PrCOCl$  yield respectively o- (58) and m-tolyl butyrate (72.6%). Physical data are given. A. Li.

**Nitrosation of phenols.** XIX. The three cresols and their methyl ethers. Some semicarbazide reactions. H. H. Hodgson and E. A. C. Crouch (*J. C.S.*, 1943, 221—223).— $HNO_2$  reacts normally with o- and m-cresol to give 5:1:2- (I) and 6:1:3- $NO$ : $C_6H_3Me$ : $OH$  (II), respectively; p-cresol similarly affords 3:1:4- $NO_2$ : $C_6H_3Me$ : $OH$ .  $NO$ : $SO_4H$  and o- $C_6H_4Me$ : $OMe$  in  $AcOH$  at 0°, then at room temp. for 3 days, yield 3:5:1:2-( $NO_2$ ) $_2$ : $C_6H_2Me$ : $OH$  (III), but at  $\Delta$ -5° give 5-nitroso-o-tolyl Me ether (IV), m.p. 53.5°. (I) and (IV) are oxidised by dil.  $HNO_3$  at 40° to (III). m- $C_6H_4Me$ : $OMe$  similarly gives 6:1:3- $NO_2$ : $C_6H_3Me$ : $OH$  (V) or 6-nitroso-m-tolyl Me ether (VI), m.p. 22°. Oxidation (dil.  $HNO_3$ ) of (II) and (VI) gives (V). (VI) and  $NH_2OH$ : $HCl$ - $NaOAc$ - $\beta$ - $C_{10}H_7$ : $OH$ -aq.  $EtOH$  afford 4-methoxy-2-methylbenzeneazo- $\beta$ -naphthol, m.p. 193°; (IV) does not react similarly. p- $NO_2$ : $C_6H_4$ : $NH$ : $NH_2$  with (IV) or (VI) gives 4'-nitro-4-methoxy-3-, m.p. 187.5°, or 4'-nitro-4-hydroxy-2-methyldi-azoaminobenzene, m.p. 205° (decomp. from 185°), respectively. With  $NH_2$ : $CO$ : $NH$ : $NH_2$ : $HCl$  and  $NaOAc$  in  $MeOH$ , (IV) yields probably 4:3:1- $OMe$ : $C_6H_3Me$ : $N(OH)$ : $N$ : $CO$ : $NH_2$ , converted by boiling  $NH_2Ph$  into 4-methoxy-3-methylhydrazobenzene-N-diazocarbonylamide, m.p. 238°, whereas (VI) affords 4-methoxy-2-methylbenzene-diazoaminocarbonylamide, m.p. 230°, unchanged by boiling  $NH_2Ph$ .

The difference in reactivity of (IV) and (VI) is ascribed to the different anionoid character of the O atoms of the NO-groups.

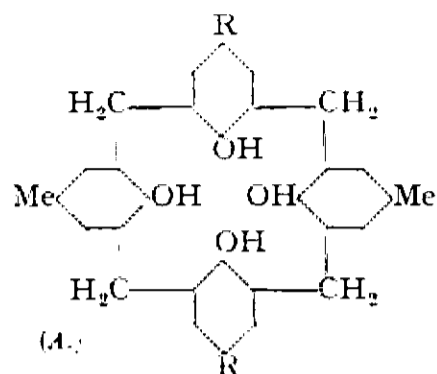
A. T. P.

**Oxidation of resorcinol by hydrogen peroxide in presence of tungstic acid sol as catalyst.**—See A., 1943, II, 217.

**Preparation of 4-nitroresorcinol.** N. B. Parekh and R. C. Shah (*J. Univ. Bombay*, 1943, 11, A, Part 5, 101—103).—2:4:1-(OH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>H with HNO<sub>3</sub> (*d* 1.42) at room temp. yields 5:2:4:1-NO<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>(OH)<sub>2</sub>·CO<sub>2</sub>H (Me ester similarly prepared), decarboxylated by AcOH-HCl-H<sub>2</sub>O in a sealed tube at 140—145° to 4:1:3-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(OH)<sub>2</sub>, m.p. 122° (cf. lit.).

A. Li.

**Indirect phenol-aldehyde condensations.** J. B. Niederl and J. S. McCoy (*J. Amer. Chem. Soc.*, 1943, 65, 629—631).—Contrary to Koebner (B., 1933, 514), 4:1:3:5-OH·C<sub>6</sub>H<sub>2</sub>Me(CH<sub>2</sub>·OH)<sub>2</sub> (I) and *p*-cresol with a little conc. HCl at room temp. (exothermic reaction rising to 63°) or with HCl gas in AcOH give a product, C<sub>32</sub>H<sub>32</sub>O<sub>4</sub>·H<sub>2</sub>O (A; R = Me), m.p. 215° (tetra-acetate, m.p. 125°). *p*-C<sub>6</sub>H<sub>4</sub>Br·OH and (I) in HCl-AcOH give a similar product (A; R = Br), m.p. 210° (tetra-acetate, m.p. 111°). The "blocked" *m*-4-xyleneol and (I) in HCl-AcOH give 3:5-di-(2'-hydroxy-3':5'-dimethylbenzyl)-*p*-cresol, m.p. 116° (triacetate, m.p. 143°). The products do not couple with *o*-C<sub>6</sub>H<sub>4</sub>Me·N<sub>2</sub>Cl.



R<sub>1</sub> S. C.

**Interconversion of hexæstrol and isohexæstrol [dimethyl ethers].** D. A. Peak and W. F. Short (*J.C.S.*, 1943, 232).—When undried H<sub>2</sub>S is passed slowly through isohexæstrol Me<sub>2</sub> ether or hexæstrol Me<sub>2</sub> ether at 305—310° (bath) interconversion occurs. isoHexæstrol is unchanged by C<sub>5</sub>H<sub>5</sub>N-piperidine at 250° and Ac<sub>2</sub>O at 250° (after hydrolysis), and is completely decomposed by H<sub>2</sub>S at 300°.

A. T. P.

**Factors determining the course and mechanism of Grignard reactions. VI. Synthesis of hexæstrol dimethyl ether (γδ-dianisylhexane).** M. S. Kharasch and M. Kleiman (*J. Amer. Chem. Soc.*, 1943, 65, 491—493).—Adding *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>EtBr (I) (prep. *in situ*) in PhMe at -80° to MgPhBr and CoCl<sub>2</sub> (5 mol.-%) in Et<sub>2</sub>O at -20° to -10° gives (*p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>Et)<sub>2</sub> (II) (41%) and Ph<sub>2</sub> (40%). Use of 15 mol.-% of CoCl<sub>2</sub> gives 27% of (II), of NiCl<sub>2</sub> (5 mol.-%) gives 14%, of FeCl<sub>3</sub> (5 mol.-%) gives 29%, but of CrCl<sub>3</sub>, MnCl<sub>2</sub>, or CuCl<sub>2</sub> (5 mol.-%) gives none. Replacing MgPhBr by pure MgMeBr (+15 mol.-% of CoCl<sub>2</sub>) gives 27% of (II). Thus, (I) and ·CoCl give *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>Et·, which then dimerises.

R. S. C.

**Formation of 3:4-dimethoxy-6-ethylphenol by the ozonisation of methyl 3:4-dimethoxy-6-ethylcinnamate.** E. Späth and M. Pailer (*Ber.*, 1940, 73, [B], 238—242).—The product of the action of HCN on 1:3:4-C<sub>6</sub>H<sub>3</sub>Et(OMe)<sub>2</sub> in presence of AlCl<sub>3</sub> and HCl is shown to be 3:4:6:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Et·CHO (I) by the formation of *m*-hemipinic acid on vigorous oxidation. (I) and CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> in AcOH at 100° afford 3:4-dimethoxy-6-ethylcinnamic acid, m.p. 169—171°. The Me ester, m.p. 96°, is transformed by ozonisation in CHCl<sub>3</sub> and treatment of the product with boiling aq. AgNO<sub>3</sub> and Zn dust into 3:4:6:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Et·CO<sub>2</sub>H, 3:4-dimethoxy-6-ethylphenol (II), b.p. 100° (bath)/0.04 mm. (benzoate, m.p. 88—90°), and (I). 2:5:4:1-(OH)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)·COMe is reduced (Zn-Hg and HCl) to 2-methoxy-5-ethylquinol, m.p. 151—153° (vac.), which is methylated to (II). It is improbable that (II) is formed from (I) by H<sub>2</sub>O<sub>2</sub> liberated during decomp. of the ozonide. It is more probable that partial decomp. of the ozonide occurs during passage of O<sub>3</sub> and the products are further changed by O<sub>3</sub>.

H. W.

**Polyhalogeno-*o*-anisidines and their derivatives.** W. S. W. Harrison, A. T. Peters, and F. M. Rowe (*J.C.S.*, 1943, 235—237).—1:2:4:5-C<sub>6</sub>H<sub>2</sub>Cl<sub>4</sub> and aq. NaOH-MeOH at 160° give 2:4:5:1-C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>·OH (I) and thence (Me<sub>2</sub>SO<sub>4</sub>-aq. NaOH) 2:4:5:1-C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>·OMe (II). (I) and HNO<sub>3</sub> (*d* 1.43)-AcOH give the 2-NO<sub>2</sub>-compound, m.p. 92—93° (lit. 81°), and (II)-HNO<sub>3</sub> (*d* 1.5) at 5—10° afford 3:4:6-trichloro-2-nitroanisole (III), m.p. 19—21°, b.p. 288°. (III) and Fe-aq. AcOH-EtOH yield 3:4:6-trichloro-*o*-anisidine (IV), m.p. 61—62°; its Ac<sub>1</sub> (AcCl-PhMe), m.p. 181—182°, or Ac<sub>2</sub> derivative (Ac<sub>2</sub>O-C<sub>5</sub>H<sub>5</sub>N), m.p. 128—129°, and HNO<sub>3</sub> (*d* 1.5) at <10° give 3:4:6-trichloro-5-nitro-*o*-acetanisidine (V), m.p. 237°, hydrolysed by H<sub>2</sub>SO<sub>4</sub> at 100° (bath) to the amine (VI), m.p. 121—122° (Ac<sub>2</sub> derivative, m.p. 142—143°). (IV) or (VI) and HNO<sub>3</sub> (*d* 1.5)-AcOH at <10° give 2:3:5-trichloro-4-nitro-6-methoxy-N-nitroaniline, m.p. 116—117° (decomp.), converted by boiling AcOH into 2:3:5-trichloro-6-methoxy-*p*-benzoquinone, m.p. 159°. Diazotised (IV) [NO·SO<sub>4</sub>H at 100° (bath)] and β-C<sub>10</sub>H<sub>7</sub>·OH in AcOH or aq. NaOH give the azo-β-naphthol, m.p. 166°. (IV) can also be diazotised through the hydrochloride (prep. by HCl-CHCl<sub>3</sub>), and after 24 hr. at 0° demethylation occurs and 3:4:6-trichlorobenzene-2-diazo-1-oxide (VII), m.p. 118° (decomp.) [also obtained from the diazonium

sulphate from (IV) and aq. NaOAc at 5—10°], is obtained. EtOH at 150° converts (VII) into (I); (VII) with alkaline β-C<sub>10</sub>H<sub>7</sub>·OH yields 2:3:5-trichloro-6-hydroxybenzeneazo-β-naphthol, m.p. 226—228°. Decomp. of the diazonium salt from 2:4:3:5:1-NH<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>ClBr<sub>2</sub>·OMe is also accompanied by demethylation, giving 4-chloro-3:5-dibromobenzene-2-diazo-1-oxide; thus halogen in position 6 is not necessary for demethylation. (VI) (diazotised, using NO·SO<sub>4</sub>H) gives 3:4:6-trichloro-5-nitrobenzene-2-diazo-1-oxide and thence 2:3:5-trichloro-4-nitro-6-hydroxybenzeneazo-2'-hydroxy-3'-naphthanilide (VIII), m.p. 285°. (VI) diazotised and coupled in AcOH, or even in AcOH-H<sub>2</sub>SO<sub>4</sub>, affords 2:3:5-trichloro-4-nitro-6-methoxybenzeneazo-2'-hydroxy-3'-naphthanilide, m.p. 282°, and a little (VIII). Reduction (Fe-aq. AcOH-EtOH at 70°) of (VI) gives 3:4:6-trichloro-2:5-diaminoanisole, m.p. 121—122° [2:5-Ac<sub>2</sub> derivative, m.p. 342° (decomp.); 2-Ac derivative, m.p. 202°, obtained by reducing (V), gives 2:3:6-trichloro-5-methoxy-4-acetamidobenzene-azo-β-naphthol, m.p. 267—268°]. 2-Diacetyl-3:4:6-trichloro-5-amino-*o*-anisidine, m.p. 142°, is obtained by reducing the corresponding 5-NO<sub>2</sub>-compound. (IV) and Br-AcOH at 15° yield 3:4:6-trichloro-5-bromo-*o*-anisidine, m.p. 101° (Ac derivative, m.p. 236—237°; azo-β-naphthol, m.p. 195°; the derived diazo-oxide yields 2:3:5-trichloro-4-bromo-6-hydroxybenzeneazo-2'-hydroxy-3'-naphthanilide, m.p. 274°). (IV) and dry Cl<sub>2</sub> in CHCl<sub>3</sub> give tetrachloro-*o*-anisidine, m.p. 95°, and thence 2:3:4:5-tetrachloro-6-methoxybenzeneazo-β-naphthol, m.p. 204°.

A. T. P.

**Action of sulphuryl and benzenediazonium chlorides on aromatic thioethers.** A. V. Rege, J. W. Airan, and S. V. Shah (*J. Univ. Bombay*, 1943, 11, A, Part 5, 83—86).—4:4'-Dihydroxy-3:3'-diacetyl- (I) and -dicarboxy- (II), and 2:2'-dihydroxy- (III) and 2:2'-dihydroxy-3:3'-dicarboxy-dinaphthyl sulphide (IV) with PhN<sub>2</sub>Cl in aq. NaOH at ~0° yield respectively 4-benzeneazo-2-acetyl-1-naphthol, m.p. 136°, 4-benzeneazo-1-hydroxy-2-naphthoic acid, 1:2-PhN<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·OH, and 1-benzeneazo-2-hydroxy-3-naphthoic acid. With SO<sub>2</sub>Cl<sub>2</sub> in C<sub>6</sub>H<sub>6</sub>, (I) and (II) yield respectively 4:2:1-C<sub>10</sub>H<sub>5</sub>ClAc·OH and 1:4:2-OH·C<sub>10</sub>H<sub>5</sub>Cl·CO<sub>2</sub>H; (III) gives no isolable product and (IV) does not react. C<sub>10</sub>H<sub>8</sub> with SO<sub>2</sub>Cl<sub>2</sub> in Et<sub>2</sub>O yields 1-C<sub>10</sub>H<sub>7</sub>Cl and 1:4-C<sub>10</sub>H<sub>6</sub>Cl<sub>2</sub>.

A. Li.

**Interaction of indene and styrene bromohydrins with sodium sulphite. Cleavage of alkali sulphonates with sodium in liquid ammonia.** C. M. Suter and H. B. Milne (*J. Amer. Chem. Soc.*, 1943, 65, 582—584).—Indene bromohydrin (I) and hot aq. Na<sub>2</sub>SO<sub>3</sub> give Na indan-2-ol-1-sulphonate (II) (83%) [characterised by conversion by Ac<sub>2</sub>O into the acetate (of the Na salt), m.p. 235—236° (corr.)] and ~2% of *trans*-indene glycol. The reaction may occur by way of indene oxide (III), since with Na<sub>2</sub>SO<sub>3</sub> this gives chiefly (II) but NaHSO<sub>3</sub> affords (at 80—90°) a mixture of *cis*- and *trans*-glycols and a little (II). Crude OH·CHPh·CH<sub>2</sub>Br (IV) with hot aq. Na<sub>2</sub>SO<sub>3</sub> gives Na β-hydroxy-β-phenylethane-α-sulphonate (V) (derived *p*-chlorobenzylthiuronium salt, m.p. 182—183°) with some OH·CHPh·CH<sub>2</sub>·OH and Ph·[CH<sub>2</sub>]<sub>2</sub>·SO<sub>3</sub>Na (VI) [derived from CH<sub>2</sub>·CHPh or CHPhMeBr present in the (IV); derived *p*-chlorobenzylthiuronium salt, m.p. 197°]. With Ac<sub>2</sub>O, (V) gives the acetate, which at 180—200° gives AcOH and CHPh·CH·SO<sub>3</sub>Na, the *p*-chlorobenzylthiuronium salt, m.p. 199°, derived therefrom being also obtained from (CHPh·CH·SO<sub>3</sub>)<sub>2</sub>Ba. Aq. NaCN and (I) give only 1-indanone and the glycols. Na in liquid NH<sub>3</sub> reduces (II) (proof of structure), (III), or (I) [by way of (III)] to 2-indanol. Na in liquid NH<sub>3</sub> reduces sulphonates containing S·C·Ar or S·C·C·CH<sub>2</sub>, but not saturated aliphatic sulphonates; e.g., CH<sub>2</sub>Ph·SO<sub>3</sub>Na gives PhMe, Na<sub>2</sub>SO<sub>3</sub>, and a little (CH<sub>2</sub>Ph)<sub>2</sub>; CHPhMe·SO<sub>3</sub>Na gives PhEt; CH<sub>2</sub>·CMe·CH<sub>2</sub>·SO<sub>3</sub>Na gives Na<sub>2</sub>SO<sub>3</sub> and (?) CH<sub>2</sub>·CMe<sub>2</sub>; but *p*-C<sub>6</sub>H<sub>4</sub>Me·CHMe·CH<sub>2</sub>·SO<sub>3</sub>Na, (V), and (VI) are unaffected.

R. S. C.

**Rôle of neighbouring groups in replacement reactions. VI. cyclo-Hexylene ethyl orthoacetate.** S. Winstein and R. E. Buckles (*J. Amer. Chem. Soc.*, 1943, 65, 613—618).—The reaction mechanisms previously indicated (A., 1943, II, 117) are confirmed. *cis*- (I) or *trans*-cyclohexane-1:2-diol (II) with CMe(OEt)<sub>3</sub> and a trace of *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>H (III) gives 65—70% of Et *cis*- (IV), b.p. 92—93°/10 mm., and *trans*-cyclohexylene Et 1:2-orthoacetate, [CH<sub>2</sub>]<sub>4</sub><CH·O>CMe·OEt, b.p. 95—96°/10 mm., respectively, yielding (I) and (II), respectively, by hydrolysis. Hydrolysis of (IV) is measured by change in the miscibility temp. of (IV)-EtOH-H<sub>2</sub>O with mineral oil; at room temp. it is very slow in NaOEt-EtOH, very rapid with (III)-EtOH, but has a half-reaction time ~25 min. in 2% AcOH. 51% of (IV) is recovered after interaction of *trans*-2-acetoxycyclohexyl *p*-toluenesulphonate with KOAc-EtOH if H<sub>2</sub>O is rigidly excluded and AcOH formed is removed. Acid hydrolysis of (IV) in aq. EtOH yields 95.5% of *cis*-2-acetoxycyclohexanol and 4.5% of (I); in AcOH containing a little H<sub>2</sub>O the yields are 92 and 8%, respectively. With (III) and Ac<sub>2</sub>O in hot AcOH, (IV) gives an ester hydrolysed to (I); with KOAc-Ac<sub>2</sub>O-AcOH, (IV) gives a product, hydrolysed to pure (II); with Ac<sub>2</sub>O-AcOH a product is obtained, which by hydrolysis yields mostly (II); Ac<sub>2</sub>O alone at 130° leads to 43% of pure *trans*-diacetate (V) and a residue, hydrolysed to (II) (cf. Post *et al.*, A., 1938, II,

(23), but at room temp. gives, after hydrolysis, mainly (I) [no (V) is formed]. With HCl-LiCl-AcOH at room temp., (IV) gives *trans*-2-chloro-1-acetoxy- (68%) and *cis*-1:2-diacetoxy-cyclohexane (32%). *trans*-2-Ethoxycyclohexanol (prep. from the oxide by  $\text{H}_2\text{SO}_4$ -EtOH; 80% yield), b.p. 86—86.5°/15 mm., with  $\text{H}_2\text{SO}_4$ -Ac<sub>2</sub>O gives the *acetate*, b.p. 91—92°/10 mm. R. S. C.

**Tervalent carbon. II. Unsymmetrical hexa-aryldimethyl peroxides.** E. L. Buhle, (Sr.) M. L. Whalen, and F. Y. Wiselogle (*J. Amer. Chem. Soc.*, 1943, 65, 584—586; cf. A., 1942, II, 13).—Treating  $\text{CPh}_3\text{Cl}$  (1 mol.) +  $\text{CAr}_3\text{Cl}$  (1 mol.) with  $\text{Hg-C}_6\text{H}_5\text{-N}_2$  for 17 hr. and oxidising the filtrate in air yields mainly  $\text{CPh}_3\text{-O}_2\text{-CAr}_3$ . This is the sole product (60—62%) when  $\text{CAr}_3\text{Cl}$  is *p*- $\text{C}_6\text{H}_4\text{Ph-CPh}_2\text{Cl}$  (I) or (*p*- $\text{C}_6\text{H}_4\text{Ph}$ )<sub>2</sub> $\text{CPhCl}$  (II), and (I) + (II) give only (65%) *diphenyl-p-xenylmethyl phenyldi-p-xenylmethyl peroxide*, m.p. 175° (instantaneous). The peroxide is formed from the free radicals, for 1 mol. each of  $\text{CPh}_3\text{Cl}$  and (*p*- $\text{C}_6\text{H}_4\text{Ph}$ )<sub>2</sub> $\text{CCl}$  (III) give mainly ( $\text{CPh}_3$ )<sub>2</sub> $\text{O}_2$  and [(*p*- $\text{C}_6\text{H}_4\text{Ph}$ )<sub>2</sub>]<sub>2</sub> $\text{O}_2$  with 13% of  $\text{CPh}_3$  *tri-p-xenylmethyl peroxide* (IV), m.p. 148°; this is because widely differing degrees of dissociation of  $\text{C}_2\text{Ar}_6$  give differing concns. of  $\text{CAr}_3$ ; thus, use of 3 mols. of  $\text{CPh}_3\text{Cl}$  and 1 mol. of (III) increases the yield of (IV) to 36%.  $\text{CPh}_3$  *diphenyl-p-xenylmethyl*, m.p. 177° (decomp.; instantaneous), and *phenyldi-p-xenylmethyl peroxide*, m.p. 186° (instantaneous), are described. Structures of the peroxides are proved by cleavage by Na-Hg, HI, or red P-I-AcOH. R. S. C.

**Preparation of methoxyphenylacetic acids.** H. A. Weidlich and M. Meyer-Delius (*Ber.*, 1940, 73, [B], 325—327).—Me 3:4-methylenedioxymandelate (I) and Zn-HCl-AcOH afford a substance,  $\text{C}_{12}\text{H}_{20}\text{O}_6$ , m.p. 256—257° (darkens) (*Me*<sub>2</sub> ester, m.p. 95—96°), and 25% of homopiperonylic acid (II), m.p. 128—129°. (II) is obtained in 96% yield from (I) and  $\text{H}_2$ -Pd-HBr-AcOH. *Me* *o*-methoxymandelate, m.p. 46°, and the *p*-isomeride are similarly hydrogenated at 55—60° and room temp., respectively, to *o*-, m.p. 124°, and *p*- $\text{OMe-C}_6\text{H}_4\text{-CH}_2\text{-CO}_2\text{H}$ , m.p. 85—86°, respectively;  $\text{BzCO}_2\text{Et}$  affords  $\text{OH-CHPh-CO}_2\text{H}$ , which is unaffected under various conditions. A. T. P.

**Effect of heat on mandelic acid.** W. R. Angus and R. P. Owen (*J.C.S.*, 1943, 249—250).— $\text{OH-CHPh-CO}_2\text{H}$  (but not its *O*-acyl derivatives or esters) undergoes change in structure and composition on being melted (the f.p. curve of mixtures of the *r*- and *l*-acids cannot thus be determined by the usual methods) probably owing to internal ester formation. The extent and products of condensation appear to be governed by the temp. and method of heating. A. T. P.

**Stability of racemates. Mandelic acid and its derivatives.** W. R. Angus and R. P. Owen (*J.C.S.*, 1943, 227—230).—M.p. or f.p. curves for mixtures of active and *r*-mandelic, acetyl- and propionyl-mandelic acids, and of Me, Et, and Bu<sup>β</sup> mandelates have been determined. Racemate stability is increased by acylation and by esterification. The f.p. of the active acids are considerably higher than those of the corresponding *r*-acids, whilst the f.p. of the *r*-esters are a few degrees higher than those of the active forms. *O*-Propionyl-*r*- (+2H<sub>2</sub>O), m.p. ~50°, anhyd. m.p. 51.2°, and *l*-mandelic acid, m.p. 70—71°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -124.5° in EtOH (vals. for other solvents given), were prepared from the mandelic acid and EtCOCl. *O*-Benzoyl-*r*-mandelic acid, m.p. 114—115°, is similarly prepared. C. R. H.

**Resolution of enantiomorphs. II. Liquid-liquid extraction.** E. Shapiro and R. F. Newton (*J. Amer. Chem. Soc.*, 1943, 65, 777—779).—Partial resolution of  $\text{OH-CHPh-CO}_2\text{H}$  (I),  $\text{OAc-CHPh-CO}_2\text{H}$  (II), *o*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-CH(OR)-CO}_2\text{H}$  (R = H and Ac), and  $\text{HCO-NH-CHPh-CO}_2\text{H}$  has been achieved by fractional distribution of the brucine salts between  $\text{H}_2\text{O}$  and  $\text{CHCl}_3$ . Multiple extractions gave a 10% resolution of (I) and (II). (I) has been partly resolved by a countercurrent extraction column. W. R. A.

**Addition of phenol ethers to substituted cinnamic acids.** B. D. Patel and K. V. Bokil (*J. Univ. Bombay*, 1943, 11, A, Part 5, 92—100).—With the appropriate phenol ethers in presence of 80%  $\text{H}_2\text{SO}_4$  at room temp.  $\text{CPhMe-CH-CO}_2\text{Et}$  yields *Et β-phenyl-β-p-anisyl-*, b.p. 210—217°/12 mm. (free acid, m.p. 100—102°; *Me* ester, b.p. 200—205°/5 mm.), *-β-p-ethoxyphenyl-*, b.p. 200—210°/8 mm. (free acid, b.p. 270—275°/20 mm.; *Me* ester, b.p. 185—195°/7 mm.), and *-β-6-methoxy-m-tolyl-butylate*, b.p. 210—218°/14 mm. (free acid, m.p. 118°; *Me* ester, b.p. 190—200°/8 mm.), *p*- $\text{C}_6\text{H}_4\text{Me-CMe-CH-CO}_2\text{Et}$  yields *Et β-p-anisyl-*, b.p. 230—235°/10 mm. (free acid, m.p. 130°; *Me* ester, b.p. 210—215°/6 mm.), *-p-ethoxyphenyl-*, b.p. 220—228°/6 mm. (free acid, m.p. 112°; *Me* ester, b.p. 210—220°/9 mm.), and *-β-6-methoxy-m-tolyl-β-p-tolyl-butylate*, b.p. 205—215°/6 mm. (free acid, m.p. 130—132°; *Me* ester, b.p. 220—225°/10 mm.; *anilide*, m.p. 140—141°), *p*- $\text{OMe-C}_6\text{H}_4\text{-CMe-CH-CO}_2\text{Et}$  yields *Et β-p-anisyl-β-p-ethoxyphenyl-*, b.p. 240—250°/11 mm. (free acid, m.p. 99—100°; *Me* ester, b.p. 245—255°/9 mm.), and *-β-6-methoxy-m-tolyl-butylate*, b.p. 245—250°/12 mm. (free acid, m.p. 120°; *Me* ester, b.p. 235—240°/9 mm.), *p*- $\text{OEt-C}_6\text{H}_4\text{-CMe-CH-CO}_2\text{Et}$  yields *Et β-ethoxyphenyl-β-6-methoxy-m-tolylbutylate*, b.p. 250—260°/8 mm. (free acid, m.p. 103—104°; *Me*

ester, b.p. 245—250°/10 mm.), *o*- $\text{OMe-C}_6\text{H}_4\text{-CMe-CH-CO}_2\text{Et}$  yields *Et β-o-anisyl-β-p-anisylbutylate*, b.p. 230—235°/10 mm. (free acid, m.p. 118—119°), and 6:3:1- $\text{OMe-C}_6\text{H}_3\text{Me-CMe-CH-CO}_2\text{H}$  (from 4:6-dimethylcoumarin and  $\text{Me}_2\text{SO}_4$  in NaOH at 50°) yields *β-p-anisyl-*, m.p. 158° (*Me* ester, m.p. 86—87°, b.p. 240—250°/20 mm.), *β-p-ethoxyphenyl-*, m.p. 148° (*Et* ester, m.p. 72°; *anilide*, m.p. 149°), and *β-6-methoxy-m-tolyl-β-4-methoxy-m-tolylbutylate*, m.p. 157° (*Et* ester, m.p. 84°; *Me* ester, m.p. 84—85°; *anilide*, m.p. 144°). *α*- and *β*- $\text{C}_{10}\text{H}_7\text{-OH}$  with  $\text{CH}_2\text{Ac-CO}_2\text{Et}$  and 80%  $\text{H}_2\text{SO}_4$  at room temp. yield respectively 4-methyl-1:2-*αβ*- (85) and -1:2-*βα*-naphthapyrone (70% yield), converted by  $\text{Me}_2\text{SO}_4$  and EtOH-NaOH into *β-1-methoxy-2-*, m.p. 137° (*Et*, b.p. 280—290°/9 mm., and *Me* ester, b.p. 280—285°/14 mm.), and *β-2-methoxy-1-naphthylcrotonic acid*, m.p. 188—189°, respectively, neither of which, like  $\text{CPh}_2\text{-CH-CO}_2\text{H}$ , adds phenol ethers under the above conditions. A. Li.

**Synthetic anthelmintics. VI. β-p-Anisyl-γ-alkylbutyrolactones.** K. Paranjape, N. L. Phalnikar, and K. S. Nargund (*J. Univ. Bombay*, 1943, 11, A, Part 5, 104—110).—*p*- $\text{OMe-C}_6\text{H}_4\text{-COPr}$ ,  $\text{CH}_2\text{Br-CO}_2\text{Et}$ , and Zn in boiling PhMe give *Et β-hydroxy-β-p-anisylhexoate*, b.p. 155°/25 mm. (free acid, b.p. 168°/25 mm.), dehydrated ( $\text{P}_2\text{O}_5$  in  $\text{C}_6\text{H}_6$ ) to *Et β-p-anisyl-Δβ-hexenoate*, b.p. 170°/20 mm., the free acid, b.p. 210°/25 mm. (*anilide*, m.p. 110°), from which (10% KOH at room temp.) with 60%  $\text{H}_2\text{SO}_4$  at room temp. yields *β-p-anisyl-γ-ethyl-γ-butyrolactone*, b.p. 185°/20 mm., demethylated ( $\text{HBr-AcOH}$ ) to the *OH-lactone*, b.p. 198°/35 mm. Similarly obtained are *β-hydroxy-β-p-anisyl-heptoic*, b.p. 190°/30 mm. (*Et* ester, b.p. 160°), *-nonoic*, b.p. 235°/45 mm. (*Et* ester, b.p. 220°/50 mm.), *-octadecoic*, m.p. 65° (*Et* ester, m.p. 58°), and *-eicosanoic acid*, m.p. 71° (*Et* ester, m.p. 60°), *β-p-anisyl-Δβ-heptenoic*, b.p. 195°/20 mm. (*Et* ester, b.p. 170°/20 mm.; *anilide*, m.p. 105°), *-nonenoic*, b.p. 240°/25 mm. (*Et* ester, b.p. 225°/45 mm.; *anilide*, m.p. 101°), *-octadecenoic*, m.p. 48° (*Et* ester, decomposes when heated; *anilide*, m.p. 68°), and *-eicosenoic acid*, m.p. 76° (*Et* ester, m.p. 68°), *β-p-anisyl-γ-propyl-*, b.p. 186°/16 mm., *-n-amyl-*, b.p. 245°/30 mm., *-tetradecyl-*, b.p. 299°/25 mm., and *-hexadecyl-γ-butyrolactone*, m.p. 58°, and *β-p-hydroxyphenyl-γ-propyl-*, b.p. 220°/35 mm., *-n-amyl-*, m.p. 44°, *-tetradecyl-*, m.p. 45°, and *-hexadecyl-γ-butyrolactone*, m.p. 78—79°. *p*-Anisyl hexyl ketone (from  $\text{C}_6\text{H}_{13}\text{-COCl}$ , PhOMe, and  $\text{AlCl}_3$ ) has b.p. 240°/50 mm. A. Li.

**Esters of dihydrochaulmoogric acid and dihydrochaulmoogryl alcohol.** K. Burschkes (*Ber.*, 1940, 73, [B], 405—408).—*Et* chaulmoograte is hydrogenated ( $\text{PtO}_2\text{-EtOH}$ ) to *Et dihydrochaulmoograte*, b.p. 210—220°/0.05 mm. [aq. NaOH-EtOH gives the free acid (I), m.p. 71°, whence ( $\text{SOCl}_2$ ) the chloride (II), b.p. 205—215°/0.1—0.2 mm.], converted by Na-EtOH at 120° (after initial reaction) into *dihydrochaulmoogryl alcohol* (III), m.p. 29—30°, b.p. 180°/0.2 mm. The appropriate alcohol and (II) in  $\text{N}_2$  give *cholesteryl* (prep. in  $\text{C}_6\text{H}_6$ ), m.p. 94°, *Δ-octadecenyl* [also from (I)], b.p. 256—270°/0.1 mm., and  $\text{CH}_2\text{Ph}$  [from (I)], b.p. 220—230°/0.2 mm., *dihydrochaulmoograte*. (III) and the respective chloride in  $\text{C}_6\text{H}_6$  and  $\text{N}_2$  afford *dihydrochaulmoogryl oleate*, b.p. 250—260°/0.15 mm., and *cinnamate*, b.p. 255—265°/0.05 mm. A. T. P.

**Peptides of dehydrogenated amino-acids.** D. G. Doherty, J. E. Tietzmann, and M. Bergmann (*J. Biol. Chem.*, 1943, 147, 617—637).—N-NaOH and acetyldehydrophenylalanine azlactone (I) are added successively to a suspension of glycine in  $\text{COMe}_2$ ; after several hr. the solution yields acetyldehydrophenylalanylglycine, m.p. 194—195°, when treated with N-HCl. The following are obtained similarly: *acetyldehydrophenylalanylphenylserine*, m.p. 226—228° (decomp.), converted by  $\text{Ac}_2\text{O}$  and anhyd. NaOAc at 40° into the azlactone (II), m.p. 184—186°, of acetyldehydrophenylalanyldehydrophenylalanine (III); *benzoyldehydrophenylalanylglycine* (IV), m.p. 208—209° (corr.); *benzoyldehydrophenylalanylphenylserine* (V), m.p. 180° (decomp.); *acetyldehydroleucylglycine*, m.p. 185—187°, by hydrolysis of the *Et* ester, m.p. 130—132°, obtained from  $\text{NH}_2\text{-CH}_2\text{-CO}_2\text{Et}$  and *acetyldehydroleucine azlactone*, b.p. 68—69°/0.15 mm. [corresponding acid, m.p. 155—157°, and its amide, m.p. 205—207° (corr.)]. *trans*-Phenylserine *Et* ester and carbobenzyloxyglycine chloride afford *carbobenzyloxyglycylphenylserine Et* ester, m.p. 149—151°, hydrolysed by NaOH-MeOH at room temp. to *carbobenzyloxyglycyl-dl-phenylserine*, m.p. 161—163°; the azlactone, m.p. 141—142°, of this substance (corresponding amide, m.p. 164—166°) yields *carbobenzyloxyglycyldehydrophenylalanine*, m.p. 168—170°. *Acetyldehydrophenylalanyl-l-alanine*, m.p. 195—196° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>25</sup> +69.6° in  $\text{C}_5\text{H}_5\text{N}$ , *l*-phenylalanine, m.p. 213—215° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>25</sup> +37.6° in  $\text{C}_5\text{H}_5\text{N}$ , and *l*-tyrosine, m.p. 228.5—229.5° (decomp.) (becomes discoloured at 221°), [ $\alpha$ ]<sub>D</sub><sup>20</sup> +45.0° in  $\text{C}_5\text{H}_5\text{N}$ , are described. Acetyl-*dl*-phenylalanylglycine is transformed by  $\text{Ac}_2\text{O}$ , PhCHO, and NaOAc into the azlactone, m.p. 206—207° (corr.), of acetyl-*dl*-phenylalanyldehydrophenylalanine, m.p. 209—211° (decomp.), softens at 206°. Similarly, acetyldehydrophenylalanylglycine gives the azlactone, m.p. 184—186° [corresponding acid, m.p. 204—205°, and amide, m.p. 229° (corr.)], of (III). (IV), PhCHO,  $\text{Ac}_2\text{O}$ , and NaOAc or (V),  $\text{Ac}_2\text{O}$ , and NaOAc yield the azlactone, m.p. 188—190°, of *benzoyldehydrophenylalanyldehydrophenylalanine*, m.p. 180—181° (decomp.) (amide, m.p. 199°). The acetylated azlactone, m.p. 193—194° (softens at 165°), of *acetyldehydrophenylalanyldehydrotyro-*

sine, m.p. 218° (decomp.), is obtained similarly. (IV),  $p$ -OH-C<sub>6</sub>H<sub>4</sub>·CHO, Ac<sub>2</sub>O, and NaOAc give the *acetylazlactone*, m.p. 231—233° (corresponding *azlactone*, m.p. 235—238°), of *benzoyldehydrophenylalanyldehydrotyrosine*, m.p. 164—166° (decomp.) [*amide*, m.p. 228° (decomp.)]. The *azlactone*, m.p. 171—173°, of *acetyldehydroleucyldehydrophenylalanine*, m.p. 215—216° (decomp.), has been prepared. *Carbobenzoyloxyglycyldehydrophenylalanyl-l-glutamic acid*, m.p. 177—179° (decomp.),  $[\alpha]_D^{20}$  -28.0 in C<sub>5</sub>H<sub>5</sub>N, and *-phenylserine*, m.p. 168—170°, are described. (II) and the required NH<sub>2</sub>-acid give *acetylbis(dehydrophenylalanyl)-glycine*, decomp. 216° after becoming discoloured at 205°, *-l-alanine*, m.p. 215—216° (decomp.),  $[\alpha]_D^{20}$  -255.1°,  $[\alpha]_D^{20}$  282.9° in C<sub>5</sub>H<sub>5</sub>N, *-l-leucine*, m.p. 235—236° (decomp.), softens at 225°,  $[\alpha]_D^{20}$  -245.6° in C<sub>5</sub>H<sub>5</sub>N, *-l-phenylalanine*, m.p. 229—230° (decomp.), darkens at 256°,  $[\alpha]_D^{20}$  -172.2° in C<sub>5</sub>H<sub>5</sub>N, *-l-tyrosine*, m.p. 172—173.5° (decomp.),  $[\alpha]_D^{20}$  -133.6° in C<sub>5</sub>H<sub>5</sub>N, *-l-proline*, m.p. 203—204° (decomp.),  $[\alpha]_D^{20}$  +60.6°,  $[\alpha]_D^{20}$  +50.6° in C<sub>5</sub>H<sub>5</sub>N, *-phenylserine*, m.p. 223—225° (decomp.), and *-l-glutamic acid*, m.p. 209—210° (decomp.),  $[\alpha]_D^{20}$  -182.6°. *-l-Cystine* and (I) give *bis(acetyldehydrophenylalanyl)-l-cystine*, m.p. 212—213° (decomp.),  $[\alpha]_D^{20}$  -19.5° in C<sub>5</sub>H<sub>5</sub>N. *Acetylbis(dehydrophenylalanyl)dehydrophenylalanine*, m.p. 233—235°, is converted into *acetyltris(dehydrophenylalanyl)-l-phenylalanine*, m.p. 201—202°, becomes yellow at 172—173°,  $[\alpha]_D^{20}$  -35.4° in C<sub>5</sub>H<sub>5</sub>N, and *-phenylserine*, m.p. 199° (decomp.); this gives *acetyltris(dehydrophenylalanyl)dehydrophenylalanine azlactone*, m.p. 247—249° (decomp.), converted into *bis(acetyldehydrophenylalanyldehydrophenylalanyl)-l-cystine*, m.p. 209—211°,  $[\alpha]_D^{20}$  -82.3°,  $[\alpha]_D^{20}$  -86.1° in C<sub>5</sub>H<sub>5</sub>N. M.p. are corr. H. W.

**Chlorination of benzoic acid.** H. G. Biswas and S. J. Das-Gupta (*J. Indian Chem. Soc.*, 1942, 19, 497—498).—BzOH with aq. KClO<sub>3</sub>-HCl affords 3 : 4 : 1- and 2 : 5 : 1-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>·CO<sub>2</sub>H, separable through their Ba salts. A. T. P.

**Ester group in polystyrene made with chloro- and bromo-benzoyl peroxides.**—See A., 1943, II, 223.

**Polymerisation of styrene in presence of 3 : 4 : 5-tribromobenzoyl peroxide.**—See A., 1943, II, 223.

**Isomorphism of organic compounds. V. Nitrobenzoic acids and substituted benzoic acids.** H. Lettré (*Ber.*, 1940, 73, [B], 386—390; cf. A., 1938, II, 324).—M.p. curves show that 1 : 1 compounds are formed from: *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and BzOH (I), *m*- (II) or *p*-C<sub>6</sub>H<sub>4</sub>Me·CO<sub>2</sub>H (III), or *m*-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H (IV); *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and (I), (II), (III), (IV), *o*-C<sub>6</sub>H<sub>4</sub>Me·CO<sub>2</sub>H, *o*-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H, *o*- or *m*-C<sub>6</sub>H<sub>4</sub>Br·CO<sub>2</sub>H, *m*-C<sub>6</sub>H<sub>4</sub>I·CO<sub>2</sub>H, or *p*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H; *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and (I), (III), or *p*-C<sub>6</sub>H<sub>4</sub>R·CO<sub>2</sub>H (R = Cl, Br, I, or OH). In the other cases investigated, mixed crystal or eutectic formation is noted. A. T. P.

**Michael reactions.** C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, 65, 437—439).—Attempts to effect Michael reactions with CH<sub>2</sub>:CH·CN (I) or CH<sub>2</sub>:CH·CO<sub>2</sub>Me (II) with NaOR-ROH led to addition of ROH. Thus, MeOH + a trace of NaOMe with (II) at 30—35° gives OMe·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>Me (77%), b.p. 137—143°, and EtOH with (I) gives *β*-ethoxypropionitrile (89%), b.p. 170—173°. However, Michael reactions with these and similar compounds proceed well in absence of a solvent, when a trace of NaOR-ROH is used at <50°. Thus, CH<sub>2</sub>Ph·CN (III) with (II) gives *γ*-carbomethoxy-*α*-phenyl- [20—23%; 24% obtained by NaNH<sub>2</sub> in an excess of (III)], b.p. 187—190°/18 mm., with CHMe·CH·CO<sub>2</sub>Et gives *γ*-carbomethoxy-*α*-phenyl-*β*-methyl- (63—68%), b.p. 170—175°/10 mm., with CMe<sub>2</sub>·CH·CO<sub>2</sub>Et affords *γ*-carbomethoxy-*α*-phenyl-*ββ*-dimethyl-, b.p. 195—200°/23 mm., with CHPh·CH·CO<sub>2</sub>Et gives *γ*-carbomethoxy-*αβ*-diphenyl-, forms, m.p. 100—101° and 59—60°, with Me<sub>2</sub> maleate give *βγ*-dicarbomethoxy-*α*-phenyl- (50%), b.p. 198—203°/10 mm., and with Et<sub>2</sub> maleate gives *βγ*-dicarbomethoxy-*α*-phenyl- (52—58%; 46% in EtOH), b.p. 185—187°/1 mm., *-butyronitrile*. With (I), (III) gives *α*-phenyl- [20—33%; 36 and 25% in Et<sub>2</sub>O and an excess of (III), respectively], b.p. 198—200°/12 mm., with CH<sub>2</sub>:CH·CH<sub>2</sub>·CN gives *α*-phenyl-*β*-methyl- (76%), b.p. 193—197°/14 mm., and with *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH:CH·CN gives *α*-phenyl-*β*-*p*-anisyl- (72%), m.p. 135—136°, *-glutaronitrile*. CHPh·CH·CN with (III) gives *αβ*-diphenyl-*glutaronitrile* (81—87%), m.p. 101—103°, with CH<sub>2</sub>Ph·CO<sub>2</sub>Et gives *γ*-carbomethoxy-*βγ*-diphenylbutyronitrile (50%), m.p. 118—121°, with *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CN gives *β*-phenyl-*α*-*p*-anisylglutaronitrile (26%), m.p. 140—142°, and with *m*-aminophenylacetone (IV), b.p. 183—187°/13 mm., gives *β*-phenyl-*α*-*m*-aminophenylglutaronitrile, forms, m.p. 120—122° (33%) and 152—154° (17%). (IV) is obtained (50—55%) from *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CN by Fe in 5% AcOH, not SnCl<sub>2</sub> or Sn-HCl, and gives a picrate, m.p. 200° (decomp.), and Ac derivative, m.p. 100—102°. R. S. C.

**3 : 4-Dimethoxyphenylsuccinic acid.** K. P. Dave, J. J. Trivedi, and K. S. Nargund (*J. Univ. Bombay*, 1943, 11, A, Part 5, 111—112).—3 : 4 : 1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO with CN·CH<sub>2</sub>·CO<sub>2</sub>Na and 10% NaOH at 40° yields *α*-cyano-*β*-3 : 4-dimethoxyphenylacrylic acid, m.p. 200° (*Me* ester, m.p. 122°), the *Et* ester, m.p. 152°, of which with aq. EtOH-KCN gives a product hydrolysed (dil. HCl) to 3 : 4-dimethoxyphenylsuccinic acid, m.p. 130° [*Me*<sub>2</sub> ester, m.p. 65°; *an-*

*hydride*, m.p. 124°, whence the *anilic*, m.p. 151°, and *p*-toluidinic acid, m.p. 158—159°, and *imide*, m.p. 172° (softens at 163°)]. A. Li.

**Diene syntheses. V. E. Lehmann** (*Ber.*, 1940, 73, [B], 304—309; cf. A., 1938, II, 488).—CH<sub>2</sub>:CH·CH<sub>2</sub>·MgBr and CH<sub>2</sub>:CH·CH<sub>2</sub>·Br-BzCl yield *phenyldiallylcarbinol* (I), b.p. 119—120°/13 mm.; *o*-tolyl-diallylcarbinol (II) has b.p. 131—132°/10 mm. (I) or (II) and SOCl<sub>2</sub>-CHCl<sub>3</sub> give the carbonyl chlorides, converted by distillation with NaOH at 270—280° into *δ*-phenyl- or *δ*-*o*-tolyl-*Δ*<sup>7/6</sup>-heptatriene, respectively, and thence by (CH<sub>3</sub>·CO)<sub>2</sub>O in C<sub>6</sub>H<sub>6</sub> at 105—110° into 3-phenyl-, m.p. 174° (slow heating) (*anhydride*, m.p. 157.5°), or 3-*o*-tolyl-3-allyl-*Δ*<sup>4</sup>-tetrahydrophthalic acid, m.p. 236—237° (previous sintering), respectively. The NaHSO<sub>3</sub> compound of 2-*m*-4'-xylyl-2-methyl-*Δ*<sup>3</sup>-tetrahydrobenzaldehyde (A., 1935, 978) and aq. KCN yield the corresponding cyanohydrin, which with HCl affords 2-*m*-4'-xylyl-2-methyl-*Δ*<sup>3</sup>-tetrahydro-mandelamide, forms, m.p. 213—214° and 158.5—159°, hydrolysed [boiling NaOH-EtOH (6 days)] to the *-mandelic acid*, m.p. 149° [Ac<sub>2</sub>O-AcOH at 100° (bath) yields the *anhydride*, forms, m.p. 105—106° and 83—83.5°], hydrogenated (Pd-BaSO<sub>4</sub>-AcOEt) to 2-*m*-4'-xylyl-2-methylhexahydromandelic acid, m.p. 182°. A. T. P.

**Alkyl *β*-nitroalkyl phthalates.**—See B., 1943, II, 211.

**Synthesis of 2 : 4-dimethoxy- and -dihydroxy-isophthalic acids.** (Miss) K. S. Radha and R. C. Shah (*J. Indian Chem. Soc.*, 1942, 19, 495—496).—3 : 2 : 4 : 1-CHO·C<sub>6</sub>H<sub>3</sub>(OMe)<sub>2</sub>·CO<sub>2</sub>H (A., 1939, II, 22) and KMnO<sub>4</sub>-10% aq. NaOH yield 2 : 4-dimethoxyisophthalic acid, m.p. 222—223° (*Me*<sub>2</sub> ester, m.p. 78—80°; 1-*Me* *H* ester, m.p. 150—151°), demethylated by AlCl<sub>3</sub> in boiling light petroleum to 2 : 4-dihydroxyisophthalic acid, m.p. 179—181°. A. T. P.

**Preparation of aldehydes by disruptive oxidation of the ethylene linking.** R. R. Davies and H. H. Hodgson (*J.S.C.I.*, 1943, 62, 90—92).—Alkaline KMnO<sub>4</sub> is preferable to CrO<sub>3</sub> for the oxidation of stilbene derivatives to aldehydes, whilst CrO<sub>3</sub> is much superior for the oxidation of R·CH:CHMe to R·CHO. Higher yields (piperonal from isosafrole; vanillin from isoeugenol) are obtained when dispersing agents are present, and this is attributed to ephemeral formation of double compounds with the aldehyde when produced.

**Ethers of protocatechualdehyde.**—See B., 1943, II, 211.

**Reaction of Grignard reagents with oximes. II. Action of aryl Grignard reagents with mixed ketoximes.** K. N. Campbell, B. K. Campbell, and E. P. Chaput. **III. Mechanism of the action of magnesium aryl halides on mixed ketoximes. New synthesis of ethyleneimines.** K. N. Campbell, B. K. Campbell, J. F. McKenna, and E. P. Chaput (*J. Org. Chem.*, 1943, 8, 99—102, 103—109; cf. A., 1939, II, 366).—II. CArAlk·N·OH (I) and MgArX (II) yield *β*-NH<sub>2</sub>-alcohols. (II) is prepared in Et<sub>2</sub>O and the solvent is removed by heating to 150—155°; PhMe is added to the residue followed by dropwise addition of (I) in PhMe at 150°. The following (m.p. of the hydrochloride and Bz derivatives, respectively, being in parentheses) are prepared thus or from COAr·CH<sub>2</sub>·NH<sub>2</sub> and (II): *β*-amino-*α*-phenyl-*α*-*p*-tolyl-, m.p. 104—105° (183—184°; 142—143°), *α*-phenyl-*α*-naphthyl-, m.p. 159—160° (232—234°; 193—194°), *α*-phenyl-*α*-*p*-anisyl-, m.p. 134° (162—163°; —), and *α*-phenyl-*α*-*p*-diphenyl-ethanol, m.p. 86—88° (220—222°; 193—195°); *β*-amino-*α*-phenyl-*α*-*p*-tolylpropanol, m.p. 74—75° (239°; 195—196°); *β*-amino-*αα*-diphenylbutanol, m.p. 77—78° (259°; 209—211°).

III. Evidence is adduced to show that ethyleneimines are intermediates in the above conversion of (I) into *β*-NH<sub>2</sub>-alcohols. If the reaction between CPhEt·N·OH and MgPhBr is effected by using a conc. Grignard reagent and hydrolysing the reaction complex with acid and ice, NH<sub>2</sub>·CHMe·CPh<sub>2</sub>·OH (III), m.p. 103—104°, is obtained in 30—40% yield. If no acid is used in the hydrolysis or if the complex is hydrolysed with acid at 0°, immediately made basic with aq. NH<sub>3</sub>, and extracted the product is 2 : 2-diphenyl-3-methylethyleneimine (IV), m.p. 74.5—75° [hydrochloride, m.p. 139—140°; picrate, m.p. 199—200°; NHPH·CS derivative, m.p. 126.5—127°; derivative, C<sub>22</sub>H<sub>15</sub>·O<sub>3</sub>N<sub>2</sub>·CO<sub>2</sub>H, m.p. 190—192°, from 3 : 1 : 2-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(CO)<sub>2</sub>O]. (IV) is isolated in better yield when the Grignard reaction is effected in PhMe at 135—145° and the complex is hydrolysed without use of acid or the acid solution kept very cold and worked up immediately. If the acid mixture is kept or allowed to get warm both (III) and (IV) are obtained. If the Grignard reaction is carried out in Et<sub>2</sub>O and the mixture hydrolysed without use of acid (IV) and much unchanged oxime result. (IV) reduces KMnO<sub>4</sub> very slowly. It is rapidly hydrolysed by warm 2N-H<sub>2</sub>SO<sub>4</sub> or 6N-HCl to (III) or to COMe·CHPh<sub>2</sub>, NH<sub>3</sub>, and (III) if the reaction is prolonged. (III) is converted by SOCl<sub>2</sub> in CHCl<sub>3</sub> followed by KOH-EtOH into (IV). MgPhBr and CPhPr·N·OH in PhMe at 150° afford 2 : 2-diphenyl-3-ethylethyleneimine, m.p. 44.5—45° (hydrochloride, m.p. 144.5—145°; 1-C<sub>10</sub>H<sub>7</sub>·NH·CO, m.p. 184—185°, and non-cryst. NHPH·CS derivative); it is hydrolysed by 3N-H<sub>2</sub>SO<sub>4</sub> to NH<sub>2</sub>·CHEt·CPh<sub>2</sub>·OH. H. W.

***αβ*-Unsaturated amino-ketones. VIII. Reaction of primary amines with 1 : 3-diketones and bromine derivatives of phenyl styryl ketone. Ethyleneimines.** N. H. Cromwell, R. D. Babson, and C. E. Harris. **IX. Colour and constitution.** N. H. Cromwell and

R. S. Johnson (*J. Amer. Chem. Soc.*, 1943, **65**, 312—315, 316—319; cf. A., 1943, II, 243).—VIII.  $\text{CH}_2\text{Bz}_2$  (1 mol.) with boiling  $\text{CH}_2\text{Ph}\cdot\text{NH}_2$  (I) or cyclohexylamine (II) (2 mols.) and a drop of conc. HCl gives *Ph*  $\beta$ -benzylamino-, m.p. 101° (*hydrobromide*, m.p. 172—174°, obtained by  $\text{HBr}\cdot\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$  and hydrolysed in  $\text{H}_2\text{O}$ ), or  $\beta$ -cyclohexylamino-, m.p. 78°, -styryl ketone, respectively, which both decolorise  $\text{Br}\cdot\text{CHCl}_3$ , are sol. in 6N-HCl, and are hydrolysed therein to  $\text{CH}_2\text{Bz}_2$ .  $\text{COMe}\cdot\text{CH}_2\text{Bz}$  gives similarly *Ph*  $\beta$ -benzylamino-, m.p. 62°, and  $\beta$ -cyclohexylamino-propenyl ketone, m.p. 54° (with  $\text{COMe}\cdot\text{CH}_2\text{Bz}$  gives an oil), sol. in dil. acids and hydrolysed therein to  $\text{COMe}\cdot\text{CH}_2\text{Bz}$ . (I) or (II) (4 mols.) with  $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{COPh}$  (1 mol.) in EtOH or  $\text{CHPh}\cdot\text{CBr}\cdot\text{COPh}$  (2 mols.) in  $\text{Et}_2\text{O}$  at 0° gives 2-benzoyl-3-phenyl-1-benzyl- (III), m.p. 108°, or -1-cyclohexyl-ethyleneimine (IV), m.p. 107°, respectively, unaffected by  $\text{Br}\cdot\text{CHCl}_3$  or  $\text{H}_2$ -Raney Ni at 50 lb.; (IV) is accompanied by a mixture, m.p. 85—90°, of, probably, (IV) and  $\text{CH}_2\text{Ph}\cdot\text{CBz}\cdot\text{N}\cdot\text{C}_6\text{H}_{11}$ .  $\text{CHPh}\cdot\text{CBr}\cdot\text{COPh}$  (1 mol.) with (I) (1 mol.) in  $\text{Et}_2\text{O}$ -light petroleum at -10° to -5° gives *Ph*  $\alpha$ -bromo- $\beta$ -benzylamino- $\beta$ -phenylethyl ketone (V), m.p. 75—77° (decomp.) [*hydrobromide* (VI), m.p. 157—159° (decomp.)], separates from  $\text{C}_6\text{H}_6$ , which generates ionic Br in EtOH- $\text{AgNO}_3$ , slowly in aq.  $\text{HNO}_3$ - $\text{AgNO}_3$ , and not in  $\text{H}_2\text{O}$ , with tetrahydroquinoline in EtOH at room temp. slowly or with  $\text{C}_6\text{H}_5\text{N}$  in warm EtOH yields (III), and in  $\text{C}_6\text{H}_6$  slowly gives (III) also. With dry  $\text{HBr}\cdot\text{C}_6\text{H}_6$ , (III) gives (VI), with dry  $\text{HCl}\cdot\text{C}_6\text{H}_6\cdot\text{Et}_2\text{O}$  at 0° or 6N-aq. HCl at 85° gives *Ph*  $\alpha$ -chloro- $\beta$ -benzylamino- $\beta$ -phenylethyl ketone hydrochloride (VII), m.p. 167—169° (decomp.), but with dry  $\text{HCl}\cdot\text{Et}_2\text{O}$  gives the hydrochloride, m.p. 129—131° (decomp.), of (III). (VII) is converted into (III) by  $\text{C}_6\text{H}_5\text{N}$  in warm MeOH, whilst (III) and boiling 15%  $\text{H}_2\text{SO}_4$  gives the betaine,  $+\text{NH}_2(\text{CH}_2\text{Ph})\cdot\text{CHPh}\cdot\text{CH}(\text{COPh})\cdot\text{O}\cdot\text{SO}_3^-$ , m.p. 218° (with small amounts of PhCHO and  $\text{COPh}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ ), insol. in  $\text{H}_2\text{O}$  or EtOH, sol. in KOH-EtOH or aq.  $\text{Na}_2\text{CO}_3$ , whence it is regenerated by acid, and converted by hot KOH-aq. EtOH into (III). In aq. HCl at 85°, (IV) gives *Ph*  $\alpha$ -chloro- $\beta$ -cyclohexylamino- $\beta$ -phenylethyl ketone hydrochloride, m.p. 187—189° (decomp.). PhCHO and 33% aq.  $\text{NH}_2\text{Me}$  give exothermally  $\text{CHPh}\cdot\text{NMe}$  (70%), b.p. 183—185°, hydrogenated (Raney Ni) in EtOH at room temp./45 lb. to  $\text{NHMe}\cdot\text{CH}_2\text{Ph}$ , b.p. 184—186°. M.p. are determined in a preheated bath.

IX. Absorption spectra of the compounds discussed above and *loc. cit.* support the structure assigned. In EtOH,  $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{COPh}$  (VIII) and  $\text{CHPh}\cdot\text{CH}\cdot\text{COPh}$  (IX) have max. at 3275 and 3350 Å. and  $\epsilon$  0.0418 and  $2.040 \times 10^{-3}$ , respectively; in  $\text{C}_6\text{H}_6$ , (IX) has a max. at 3275 Å. and  $\epsilon$   $1.468 \times 10^{-3}$ . NHR at  $\text{C}_{(a)}$  of (IX) gives visible colour and absorption at 3500—4100 Å. with a max. at  $\sim 4000$  Å. and  $\epsilon$   $2-3 \times 10^{-3}$  in EtOH, the max. being at shorter  $\lambda$  and  $\epsilon$  slightly increased in  $\text{C}_6\text{H}_6$ . NHR at  $\text{C}_{(b)}$  of (IX) has little effect on colour or the position of the max. but greatly increases  $\epsilon$  ( $14-20 \times 10^{-3}$  at 3500 Å.).  $\alpha$ -Br in (IX) has little effect on the position of the max. but decreases  $\epsilon$  ( $0.876 \times 10^{-3}$  at 3300 Å.), but simultaneous presence of NRR' at  $\text{C}_{(b)}$  has great effect ( $\epsilon$   $18.5 \times 10^{-3}$  at 4025 Å.). Absorption of the imines closely resembles that of (VIII); e.g., (III) has a max. at 3275 Å. and  $\epsilon$   $0.0623 \times 10^{-3}$  in EtOH. Resonance accounts for most of these results. R. S. C.

Polymethylbenzoylnaphthoic acids. R. H. Martin (*J.C.S.*, 1943, 239—241).—1:2- $\text{C}_{10}\text{H}_8(\text{CO}_2\text{O})$  (I), 1:2:3- $\text{C}_6\text{H}_3\text{Me}_3$  (II) (excess), and  $\text{AlCl}_3$  at room temp. give 1-(3':4':5'-trimethylbenzoyl)-2-naphthoic acid (III), m.p. 273—274° [ $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$  gives the acetoxylactone (IV),  $\text{C}_{23}\text{H}_{20}\text{O}_4$ , m.p. 231—232°, hydrolysable to (III)], and 2-(3':4':5'-trimethylbenzoyl)-1-naphthoic acid (V), m.p. 191—192° (acetoxylactone, m.p. 161.5—162.5°; benzoyloxylactone, m.p. 191.5—192.5°). (III) or (V) with KOH at 260—280° or 280—340° gives 3:4:5:1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$  and 2- or 1- $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$ , respectively. 2:1- $\text{C}_{10}\text{H}_8\text{Me}\cdot\text{COCl}$  and (II)- $\text{AlCl}_3\cdot\text{CS}_2$  at 0°, then at room temp., give 1-(3':4':5'-trimethylbenzoyl)- (VI), m.p. 150—151°, and 1-(2':3':4'-trimethylbenzoyl)-2-methylnaphthalene, m.p. 108—108.5°. (VI) and  $\text{SeO}_2\cdot\text{H}_2\text{O}$  at 235°, followed by  $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ , yield (IV). (I), 1:2:3:4- $\text{C}_6\text{H}_2\text{Me}_4$ ,  $\text{AlCl}_3$ , and  $\text{PhNO}_2$  at 0° (12 hr.), then at room temp. (60 hr.) afford 2-(2':3':4':5'-tetramethylbenzoyl)-1-naphthoic acid, m.p. 241.5—242.5°, converted by  $\text{BzCl}$  and a little conc.  $\text{H}_2\text{SO}_4$  at 100° (bath) into (probably) 5:6:7:8-tetramethyl-1:2-benzanthraquinone, m.p. 203—203.5°. Prep. of 1:2:3:4- $\text{C}_6\text{H}_2\text{Me}_3\text{Br}$  is modified; 1:2:3:4- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{MgBr}$  and (I) give a difficultly separable mixture of acids. A. T. P.

Alkylation of ethyl 3-methyl- $\Delta^2$ -cyclohexenone-4-carboxylate (Hagemann's ester) and related substances. L. I. Smith and G. F. Rouault (*J. Amer. Chem. Soc.*, 1943, **65**, 631—635).—Adding piperidine to  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  (2 mols.) and paraformaldehyde (1 mol.) with cooling, heating at 100°, and treating the resulting crude  $\text{Et}_2$  3-methyl- $\Delta^2$ -cyclohexenone-4:6-dicarboxylate (I) with boiling  $\text{NaOEt}\cdot\text{EtOH}$  (1 mol.; 2 mols. give 10%) gives Et 3-methyl- $\Delta^2$ -cyclohexenone-4-carboxylate (II) (40—50%), b.p. 142—144°/15 mm. [semicarbazone, m.p. 165—167° (lit. 169°)] (cf. A., 1896, i, 393; 1939, II, 412). In boiling aq.  $\text{H}_2\text{SO}_4$ , (I) gives 3-methyl- $\Delta^2$ -cyclohexenone (III) (24%); b.p. 75—77°/10 mm., in  $\text{H}_2\text{SO}_4\cdot\text{AcOH}\cdot\text{H}_2\text{O}$  gives (III) (44%) and (II) (8%), and in  $\text{H}_2\text{O}$  at 200° gives (III) (25%) and (II) (21%).  $\text{NaOMe}\cdot\text{MeI}\cdot\text{MeOH}$  at 5°, later 20°, and finally the b.p. converts (II) into 2:3-dimethyl- $\Delta^2$ -cyclohexenone

(IV) (37%), b.p. 90—96°/14 mm. [semicarbazone, sinters 200—205°, m.p. 222° (lit. 225°)], and its 4- $\text{CO}_2\text{Et}$ -derivative (V) (17%), b.p. 138—142°/12 mm.; MeBr at <10° gives 49% of (IV). EtBr, (II), and NaOEt in boiling EtOH give the 4- $\text{CO}_2\text{Et}$ -derivative (55%) (VI), b.p. 141—143°/9 mm. (semicarbazone, m.p. 160—164°), of 3-methyl-2-ethyl- $\Delta^2$ -cyclohexenone (VII) (27%), b.p. 82—85°/9 mm. (semicarbazone, m.p. 190—194°) [obtained from (VI) in 62% yield by KOH-EtOH]. Perhydrogeranyl bromide, (II), and NaOEt in boiling EtOH give only (49%) Et 3-methyl-2-perhydrogeranyl- $\Delta^2$ -cyclohexenone-4-carboxylate, b.p. 182°/4 mm. (semicarbazone, m.p. 85.5—87°, formed slowly), and thence (KOH-EtOH) 3-methyl-2-perhydrogeranyl- $\Delta^2$ -cyclohexenone (54%), b.p. 153—154°/3 mm. (semicarbazone, m.p. 93—95°). Condensing  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  with MeCHO by piperidine at the b.p. and hydrolysing the product by 25% (vol.)  $\text{H}_2\text{SO}_4$  gives 3:5-dimethyl- $\Delta^2$ -cyclohexenone (19%), b.p. 81°/9 mm, its 4- $\text{CO}_2\text{Et}$ - (6%), b.p. 146°/12 mm., and 4:6-( $\text{CO}_2\text{Et}$ ) $_2$ -derivative (a little), b.p. 205°/11 mm. Pd-C d (A., 1940, II, 351) at 200° converts (IV) into *o*-3-xenol (53%), but other reagents were unsuccessful. R. S. C.

Reactions catalysed by aluminium chloride. XIX. Synthesis of stereoisomeric 1-keto-9-methyldecahydronaphthalenes. C. D. Nenitzescu, E. Ciorănescu, and V. Przemetzky (*Ber.*, 1940, **73**, [B], 313—315; cf. A., 1939, II, 268).— $\text{CO}_2\text{Me}\cdot[\text{CH}_2]_2\cdot\text{COCl}$ , 1-methyl- $\Delta^1$ -cyclohexene, and  $\text{AlCl}_3$  in  $\text{PhNO}_2$  at room temp. (2 days) give Me  $\gamma$ -keto- $\gamma$ -2-methyl- $\Delta^1$ -cyclohexenylbutyrate, b.p. 150—160°/15 mm., converted by  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}\cdot\text{NaOEt}\cdot\text{EtOH}$  at 180° into  $\gamma$ -2-methyl- $\Delta^1$ -cyclohexenylbutyric acid (I), b.p. 159—160°/9 mm., 175°/20 mm. [*p*-bromophenacyl ester, m.p. 78° (lit. 65—66°)]. Prolonged warming with alkali causes migration of the double linking in (I), and the product then affords a colourless NN'-di-*p*-dimethylaminophenyl-carbamide, m.p. 148° (cf. Zetzsche *et al.*, A., 1939, II, 467). The chloride of (I) with  $\text{AlCl}_3$  in cyclohexane at 0°, then at room temp., and finally at 40°, yields (cf. Linstead *et al.*, A., 1938, II, 268) *cis*-, b.p. 92—93°/5 mm. [semicarbazone, m.p. 223° (decomp.)], and *trans*-8-methyl-1-ketodecahydronaphthalene, b.p. 82—83°/5 mm. (semicarbazone, m.p. 185°). A. T. P.

Oxidation of cholesterol. Isolation of 1-keto-2:13-dimethyl- $\Delta^9$ : $^{14}$ -dodecahydro-7-phenanthrol.—See A., 1943, II, 235.

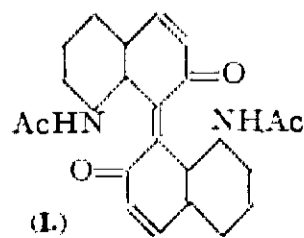
Monomeric fluorenone peroxide. G. Wittig and G. Pieper (*Ber.*, 1940, **73**, [B], 295—297; cf. A., 1939, II, 22).—Fluorenone (I) and  $\sim 1.5\text{N}\cdot\text{Et}_2\text{O}\cdot\text{H}_2\text{O}_2 + \text{P}_2\text{O}_5$  at room temp. give the monomeric fluorenone peroxide (II),  $\text{C}_{12}\text{H}_8>\text{C}\cdot\text{O}\cdot\text{O}\cdot\text{C}$ , m.p. 108—108.5°, converted by  $\text{Ac}_2\text{O}\cdot\text{AcOH}\cdot\text{H}_2\text{SO}_4$  at 0° for 48 hr. into (I) and the lactone, m.p. 94—95° [also obtained from (I) and  $\text{Ac}_2\text{O}\cdot\text{H}_2\text{O}_2\cdot\text{H}_2\text{SO}_4$ ], of *o*-OH- $\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}\cdot\text{o}$ . A. T. P.

Condensation of acyloins with ethyl acetate. R. B. Woodward and E. R. Blout (*J. Amer. Chem. Soc.*, 1943, **65**, 562—565).—Adding  $\text{Pr}^n\text{CO}_2\text{Et}$  and then EtOAc to Na wire in  $\text{Et}_2\text{O}$ , evaporating, and heating the residue at 100° gives 2-ethyl-4-*n*-propylcyclopentane-1:2-dione (I) (32%), m.p. 119.4—120.5°. This structure, contrary to that proposed by Bouveault *et al.* (A., 1907, i, 479; 1910, i, 92), is proved by rapid neutralisation of 1 NaOH, formation of a reddish-violet colour with  $\text{FeCl}_3$  (enolisation), and similarity of its absorption (max. at 255 m $\mu$ ;  $\log \epsilon$  4.12) in EtOH to that (max. at 258 m $\mu$ ;  $\log \epsilon$  4.08) of dimethyldihydroresorcinol. The autoxidation of (I) in air is characteristic of alkyl-substituted cyclic  $\beta$ -diketones. The other reactions (*loc. cit.*) of (I) are also explained by this structure and analogous structures apply to the other products described by Bouveault *et al.* The condensation involves the reactions,  $\text{OH}\cdot\text{CHPr}^n\cdot\text{CO}\cdot\text{CHEt}\cdot\text{COMe} \rightleftharpoons \text{COPr}^n\cdot\text{CH}(\text{OH})\cdot\text{CHEt}\cdot\text{COMe} \rightarrow$  3-hydroxy-2-ethyl-4-*n*-propyl- $\Delta^4$ -cyclopentenone  $\rightarrow$  (I). R. S. C.

Electrolytic preparation of quinhydrone. R. E. Ely (*Ind. Eng. Chem. [Anal.]*, 1943, **15**, 284—285).—Quinol is oxidised electrolytically in  $\text{H}_2\text{O}$  to a 75% yield of 98% pure quinhydrone. J. D. R.

Effects of environment and aggregation on absorption spectra of dyes.—See A., 1943, I, 192.

Dinaphthones. A. Rieche and W. Rudolph (*Ber.*, 1940, **73**, [B], 335—342).—8:2-NHAc- $\text{C}_{10}\text{H}_8\cdot\text{OH}$  and aq.  $\text{FeCl}_3\cdot\text{HCl}$  (or  $\text{CuO}\cdot\text{PhNO}_2$ ) at 70° afford 1:1'-(8:8'-diacetamido-2:2'-dinaphthone) (I), m.p. 332° (phenylhydrazone, m.p. 314°), reduced (Zn in aq. NaOH or AcOH) to 8:8'-diacetamido-2:2'-dihydroxy-1:1'-dinaphthyl (II), m.p. 289—290°;  $\text{Me}_2\text{SO}_4$  then yields (probably) the 2:8:2':8'- $\text{Me}_4$  derivative, m.p. 244—245°. (II) is reconverted into (I) by  $\text{K}_3\text{Fe}(\text{CN})_6$ -aq. NaOH, and with conc. HCl at 180° affords 1:1'-dinaphthylene-2:8'-2':8-dioxide (III), m.p. 242°. 8:2- $\text{C}_{10}\text{H}_8\text{Cl}\cdot\text{OH}$  and aq.  $\text{K}_3\text{Fe}(\text{CN})_6$ -NaOH yield impure 1:1'-(8:8'-dichloro-2:2'-dinaphthone), m.p. 168—193°, converted by aq.  $\text{Na}_2\text{S}_2\text{O}_4\cdot\text{NaOH}$  at 70°, through the corresponding dinaphthol, into (III). 8:2-NHAc- $\text{C}_{10}\text{H}_8\cdot\text{OH}$  and  $\text{Ac}_2\text{O}\cdot\text{NaOAc}\cdot\text{AcOH}$  give 8-acetamido-2-acetoxynaphthalene (IV), m.p. 184°, and (excess of  $\text{Ac}_2\text{O}$ ) some  $\text{Ac}_3$  compound, m.p. 98—99°. (IV) and  $\text{SO}_2\text{Cl}_2\cdot\text{C}_6\text{H}_6$  yield 8:5:7:2-NHAc- $\text{C}_{10}\text{H}_4\text{Cl}_2\cdot\text{OAc}$ , m.p. 212°, hydrolysed by aq.



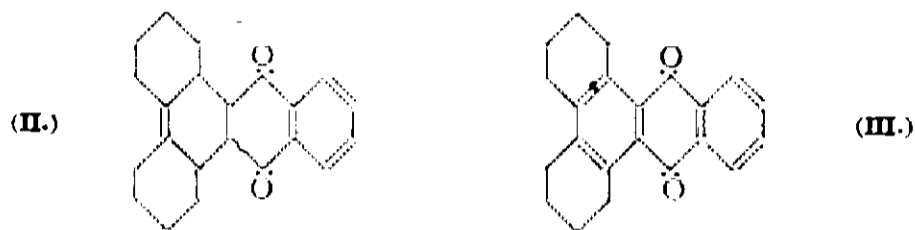
NaOH to 5 : 7-dichloro-8-acetamido-2-naphthol, m.p. 263°, which is oxidised by aq.  $K_3Fe(CN)_6$ -aq. NaOH at 90° to 1 : 1'-(5 : 7 : 5' : 7'-tetrachloro-8 : 8'-diacetamido-2 : 2'-dinaphthone), m.p. 304° (decomp.). 2 : 7 : 8-(OH) $_2$ C $_{10}$ H $_5$ ·NHAc and aq.  $FeCl_3$ -HCl at 70° afford 1 : 1'-(8 : 8'-diacetamido-7 : 7'-dihydroxy-2 : 2'-dinaphthone), m.p. 310°.

A. T. P.

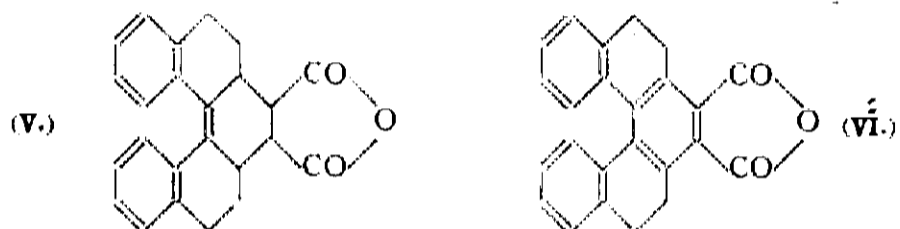
**Aromatic hydrocarbons and their derivatives. XXX. Syntheses in the perylene series.** E. Clar (*Ber.*, 1940, 73, [B], 351—353; cf. A., 1940, II, 273).—1- $\beta$ -Naphthoxyanthraquinone and  $AlCl_3$ -NaCl at 140°, then at 200°, give 12 : 6'-oxido-1' : 2' : 1 : 2-benzperylene (I), m.p. 280—281°, and 12 : 6'-oxido-1' : 2' : 1 : 2-benzperylene-3 : 10-quinone (II), C $_{24}$ H $_{10}$ O $_3$ ; (II) is also obtained by oxidising (I) with  $CrO_3$  or, better, with air in AcOH or xylene. When O $_2$  is passed through the above  $AlCl_3$  melt, (II) is obtained, with a little (I). (I) forms an adduct with ( $\cdot$ CH·CO) $_2$ O much more readily than perylene.

A. T. P.

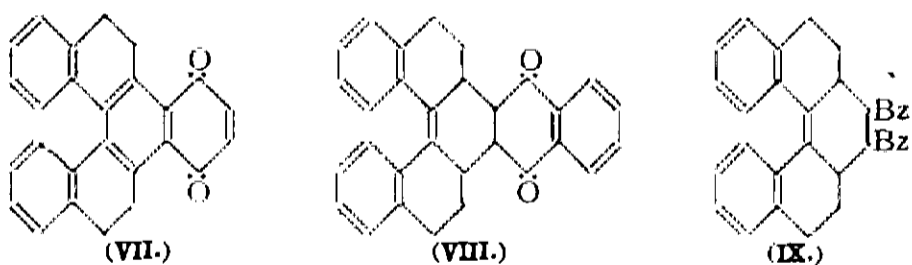
**Mechanism of the diene reaction.** F. Bergmann, H. E. Eschinazi, and M. Neeman (*J. Org. Chem.*, 1943, 8, 179—188).—Dicyclohexenyl (I) and  $p$ -O·C $_6$ H $_4$ ·O (5 : 1) at 100° afford isomeric adducts, C $_{30}$ H $_{40}$ O $_2$ , m.p. 247° and 212°, converted by KOH-EtOH at room temp. into enols, m.p. 327° and 310—312°, respectively. (I) and 1 : 4-naphthaquinone (5 : 1) at 100° afford the substance (II), m.p. 207—208°, converted by KOH-EtOH into a quinone, m.p. 248°, and by AcOH-conc. HBr into the compound (III), m.p. 234—235°. Fumaric



acid and (I) do not react at 100° but at 190—200° yield an adduct identified as the dianilide, C $_{28}$ H $_{22}$ O $_2$ N $_2$ , m.p. 312°. The adduct, C $_{20}$ H $_{26}$ O $_2$ N, m.p. 187°, is obtained from (I) and  $\beta$ -nitrostyrene; it does not undergo catalytic hydrogenation. With CO(CH $_2$ CHPh) $_2$  at 180—190° (I) yields the double adduct, C $_{41}$ H $_{50}$ O, m.p. 208—209°.



Maleic anhydride and 3 : 4 : 3' : 4'-tetrahydro-1 : 1'-dinaphthyl (IV) give the adduct (V), m.p. 256°, converted by CH $_2$ N $_2$  into the corresponding Me $_2$  ester, m.p. 168°, which is isomerised and hydrolysed by boiling BuOH-NaOBu to an acid, m.p. 239°; a second isomeric



adduct, m.p. 260°, is formed in small amount. Condensation in boiling PhNO $_2$  leads to the substance (VI), m.p. 275°. (IV) and  $p$ -O·C $_6$ H $_4$ ·O at 125—150° afford the substance (VII), m.p. 268°, which is unchanged by HBr-AcOH. (IV) and 1 : 4-naphthaquinone (1 : 2) at 130° give the adduct (VIII), m.p. 226°. *trans*-( $\cdot$ CHBz) $_2$  and (IV) do not react in boiling C $_6$ H $_6$  but at 200° the compound (IX), m.p. 236—238°, is slowly formed; it is dehydrated by boiling Ac $_2$ O containing H $_3$ PO $_4$  ( $d$  1.75) to the corresponding furan, C $_{36}$ H $_{26}$ O, m.p. 272—273°.

H. W.

#### IV.—STEROLS AND STERIOD SAPOGENINS.

**Oxidation of cholesterol. Isolation of 1-keto-2 : 13-dimethyl- $\Delta^9$ : $^{14}$ -dodecahydro-7-phenanthrol and preparation of derivatives.** H. Köster and W. Logemann (*Ber.*, 1940, 73, [B], 298—304).—The product obtained from the mother-liquors after oxidising cholesteryl acetate dibromide and separating dehydroandrosterone and pregnenolone acetates is heated with dil. H $_2$ SO $_4$ ; the resulting compound with Ac $_2$ O at 120° for 2 hr. affords 1-keto-2 : 13-dimethyl- $\Delta^9$ : $^{14}$ -dodecahydro-7-phenanthryl acetate, (I), m.p. 128—129°, [ $\alpha$ ] $_D^{20}$  -87° [oxime, m.p. 166—169°; semicarbazone, m.p. 243° (decomp.)], hydrolysed (aq. H $_2$ SO $_4$ -MeOH at 50—60°) to 1-keto-2 : 13-dimethyl- $\Delta^9$ : $^{14}$ -dodecahydro-7-phenanthrol (II), m.p. 133—134°, [ $\alpha$ ] $_D^{20}$  -88°. Hydrogenation (1.6 mols. of H $_2$ ; PtO $_2$ -AcOH) of (I) (followed by oxidation with  $CrO_3$ -90% AcOH) gives the acetate, m.p. 144—145°, [ $\alpha$ ] $_D^{20}$  -12.2° (oxime, m.p. 154—156°), of 1-keto-2 : 13-dimethylperhydro-7-phenanthrol, m.p. 128—129° (3 : 5-dinitrobenzoate, m.p. 192—

193.5°); these are probably identical with the compounds obtained from  $\beta$ -ergostenyl acetate by Achtermann (A., 1934, 1000). (II) and  $Al(OPr^i)_3$  in boiling PhMe-cyclohexanone yield 1 : 7-diketo-2 : 13-dimethyl- $\Delta^9$ : $^{14}$ -dodecahydrophenanthrene, m.p. 140—141°, [ $\alpha$ ] $_D^{20}$  +128°. (I) and boiling  $MgMeI$ -C $_6$ H $_6$ -Et $_2$ O afford 1 : 7-dihydroxy-1 : 2 : 13-trimethyl- $\Delta^9$ : $^{14}$ -dodecahydrophenanthrene, m.p. 162.5—163°, oxidised by  $Al(OPr^i)_3$ -PhMe-cyclohexanone to 7-keto-1 : 2 : 13-trimethyl- $\Delta^9$ -dodecahydro-1-phenanthrol (III), m.p. 195.5—196.5°, [ $\alpha$ ] $_D^{20}$  +94.1°. CH $_2$ :CK (prep. in liquid NH $_3$ ) with (I) in C $_6$ H $_6$ -Et $_2$ O yields 1 : 7-diketo-2 : 13-dimethyl-1-acetylenyl- $\Delta^9$ : $^{14}$ -dodecahydrophenanthrene, m.p. 217—218.5°, [ $\alpha$ ] $_D^{20}$  -108.5°, converted by  $Al(OPr^i)_3$  into 7-keto-2 : 13-dimethyl-1-acetylenyl- $\Delta^9$ -dodecahydro-1-phenanthrol (IV), m.p. 131—132°, [ $\alpha$ ] $_D^{20}$  +77.7°. [ $\alpha$ ] are in CHCl $_3$ . (III) and (IV) have no physiological activity.

A. T. P.

**Dehydration of cholesterol in liquid sulphur dioxide.** R. H. Levin (*J. Amer. Chem. Soc.*, 1943, 65, 627—628).—In (liquid) SO $_2$  at 100—140°, cholesterol gives 9—33% of dicholesteryl ether, m.p. 203—205° (cf. lit.) [tetrabromide, m.p. 164—166° (decomp.)]. Presence of anhyd. CuSO $_4$  gives 54% at 100° and 40% at 135°, of CuSO $_4$ ·5H $_2$ O gives 76% at 100° but resins at 135°, of powdered glass gives 29% (remainder resinified), of CuCl $_2$  gives 26%, and of S gives 18%. Cu, Raney Ni, FeSO $_4$ , CaSO $_4$ , and Na $_2$ CO $_3$ -Cu $_3$ (PO $_4$ ) $_2$  inhibit the reaction.

R. S. C.

**Bile acids and related substances. XX. Attempted preparation of  $\Delta^9$ -cholenic acid.** H. B. Alther and T. Reichstein (*Helv. Chim. Acta*, 1943, 26, 492—511; cf. A., 1938, II, 497).—Me 12( $\beta$ )-hydroxy- is oxidised by  $CrO_3$  in AcOH at 18° to Me 12-keto-cholanate, m.p. 107—108°, [ $\alpha$ ] $_D^{16}$  +87.7°  $\pm$  1° in COMe $_2$ ; a form of m.p. 152° (Ohta, A., 1939, II, 371) has not been encountered. It is hydrolysed and then brominated in AcOH (stable to  $CrO_3$ ) to a mixture of acids separated by Et $_2$ O into 11( $\alpha$ )- (II), m.p. 196—197° (decomp.), [ $\alpha$ ] $_D^{15}$  +31.9°  $\pm$  2° in CHCl $_3$ , [Me ester (III), m.p. 60—64°, [ $\alpha$ ] $_D^{19}$  +26.6°  $\pm$  2° in COMe $_2$ ], and 11( $\beta$ )- (IV), m.p. 171—174° (decomp.), [ $\alpha$ ] $_D^{15}$  +16.3°  $\pm$  2° in CHCl $_3$ , -bromo-12-ketocholanic acid. (IV) yields a Me ester (V), m.p. 77—79°, [ $\alpha$ ] $_D^{17}$  +19.8°  $\pm$  2° in COMe $_2$ , also isolable when the crude acid is used. (V) and boiling C $_5$ H $_5$ N afford Me 12-keto- $\Delta^9$ -cholenate (VI), m.p. 89—90°, [ $\alpha$ ] $_D^{20}$  +93.1°  $\pm$  2° in MeOH, which when pure invariably separates as needles from the slowly cooling solutions but, when crude, sometimes gives leaflets, m.p. 72—74°. Its prep. is rendered difficult by a very tenacious impurity and its homogeneity is best judged by the height of the absorption max. in the ultra-violet. The prep. of (VI) from (III) and boiling C $_5$ H $_5$ N, collidine, or NaOAc and from mixtures of (III) and (V) is described. 12-Keto- $\Delta^9$ -cholenic acid has m.p. 145—146°. Hydrogenation (PtO $_2$  in AcOH) of (VI) gives a mixture of Me cholanate and Me 12( $\beta$ )-hydroxycholanate. Reduction of crude (VI) by N $_2$ H $_4$ ·H $_2$ O and NaOEt at 170° with subsequent methylation affords a mixture of Me cholanate (VII) and  $\Delta^9$ - (VIII) and  $\Delta^{11}$ -cholenate (IX) whereas pure (VI) yields a mixture of (VIII) and (IX). BzO $_2$ H in CHCl $_3$  oxidises crude (VIII) to Me 11 : 12-, m.p. 97—98° [from (IX)], and a Me 9 : 11-oxidocholanate, m.p. 74.5—76°, [ $\alpha$ ] $_D^{13}$  +18.8°  $\pm$  2° in COMe $_2$ ; the last with boiling H $_2$ SO $_4$ -MeOH followed by CH $_2$ N $_2$  gives a (?) Me cholidienate, m.p. 88—90°, and with boiling AcOH affords a substance, m.p. 184—198°. Reduction (H $_2$ , PtO $_2$ , AcOH) of (VIII) + (IX) gives (VII). M.p. are corr. (block); limit of error  $\pm$  2°.

H. W.

**Bile acids and related substances. XIX. Methyl 3( $\alpha$ )-hydroxy- $\Delta^{11}$ -norcholenate and 3( $\alpha$ )-hydroxy- $\Delta^{11}$ -bisorcholenate.** P. Grandjean and T. Reichstein (*Helv. Chim. Acta*, 1943, 26, 482—492).—Me 3( $\alpha$ )-hydroxy- $\Delta^{11}$ -cholenate and  $MgPhBr$  give the non-cryst. carbinol which with Ac $_2$ O-C $_5$ H $_5$ N at 18° affords diphenyl-3( $\alpha$ )-acetoxyl- $\Delta^{11}$ -norcholenylcarbinol (I), m.p. 151—153°, [ $\alpha$ ] $_D^{14}$  +47.3°  $\pm$  3° in COMe $_2$ . (I) is dehydrated by boiling AcOH to diphenyl-3( $\alpha$ )-acetoxyl- $\Delta^{11}$ -bisorcholenylethylene (II), m.p. 142—143°. Successive treatments of (I) with Br-CHCl $_3$ ,  $CrO_3$ -AcOH, and Zn dust-AcOH give mainly (II) with little acid. Me 3( $\alpha$ )-acetoxyl- $\Delta^{11}$ -norcholenate (III), m.p. 133—134°, [ $\alpha$ ] $_D^{15}$  +56.2°  $\pm$  2° in COMe $_2$ , is best obtained by direct oxidation of (II) by excess of  $CrO_3$  followed by esterification (CH $_2$ N $_2$ ) and re-acetylation. (III) is hydrogenated (PtO $_2$  in AcOH) to Me acetylnorlithocholate, m.p. 159—160°, and converted by HCl-MeOH in CHCl $_3$  at 18° into Me 3( $\alpha$ )-hydroxy- $\Delta^{11}$ -norcholenate (IV), m.p. 140—141°. (IV) and  $MgPhBr$  afford the non-cryst. carbinol; the non-cryst. acetate is dehydrated by boiling AcOH to the resinous diphenyl-3( $\alpha$ )-acetoxyl- $\Delta^{11}$ -ternorcholenylethylene. This is oxidised by  $CrO_3$  and the acidic portion methylated and acetylated to Me 3( $\alpha$ )-acetoxyl- $\Delta^{11}$ -bisorcholenate, m.p. 99—100°, [ $\alpha$ ] $_D^{12}$  +10.7°  $\pm$  2° in COMe $_2$ . Me 3( $\alpha$ )-hydroxy- $\Delta^{11}$ -bisorcholenate has m.p. 107—108°. M.p. are corr. (block); limit of error  $\pm$  2°.

H. W.

**Bile acids and related substances. XXII. 11-Keto- and 11( $\alpha$ )-hydroxy-cholanic acid.** H. Reich and T. Reichstein (*Helv. Chim. Acta*, 1943, 26, 562—585).—Me  $\Delta^{11}$ -cholenate (I) is converted by HOBr into a difficultly separable mixture (II) of substances which is therefore directly oxidised ( $CrO_3$ ) and then debrominated (Zn dust). Chromatographic ( $Al_2O_3$ ) fractionation of the product leads to a little (I), mainly Me 11-ketocholanic acid (III), m.p. 88—89°, [ $\alpha$ ] $_D^{19}$  +46.0°  $\pm$  1° in COMe $_2$ , and Me 12-keto- $\Delta^9$ -cholenate, m.p. 88—90°.

The change can be effected by HOBr in aq. Bu<sup>o</sup>OH or, more conveniently, by NHAcBr in aq. Bu<sup>o</sup>OH or aq. COMe<sub>2</sub>. HOCl or chloramine-T in presence of a trace of acid may also be used whereby similar intermediates with Cl for Br are formed. The constitution of (III) is established from the known position of the double linking in (I) and the non-identity of (III) and Me 12-ketocholanate. CO in (III) is very non-reactive and cannot be detected by the usual reagents, but (III) is slowly hydrogenated (PtO<sub>2</sub> in AcOH) to Me 11(a)-hydroxycholanate (IV), m.p. 87—88°, [α]<sub>D</sub><sup>20</sup> +49.8° ± 2° in COMe<sub>2</sub>, quantitatively reoxidised (CrO<sub>3</sub>) to (III). The most conclusive preliminary evidence of the configuration of (IV) is found in attempts to separate (II) chromatographically with very active Al<sub>2</sub>O<sub>3</sub>, which yield Me 11:12-dibromocholanate, Me 11(a):12(a)-oxidocholanate (V), m.p. 64.5—65.5°, [α]<sub>D</sub><sup>20</sup> +47.5 ± 9° in COMe<sub>2</sub>, and an amorphous Br-compound, probably Me 9:11-dibromo-12-hydroxycholanate. (V) differs from the 11(β):12(β)-ester obtained by oxidising (I) with CrO<sub>3</sub>. Hydrogenation (Raney Ni) of (V) gives Me cholanate and (IV). (IV) is slowly transformed by Ac<sub>2</sub>O in C<sub>5</sub>H<sub>5</sub>N at 100° into a non-cryst. acetate and by AcOH-HCl into a mixture mainly of (I) and Me Δ<sup>9</sup>-cholenate, leaflets, m.p. 49.5—50°, or needles, m.p. 67—67.5°, [α]<sub>D</sub><sup>18</sup> +39.15° ± 1° in COMe<sub>2</sub> [most conveniently obtained from (IV) and POCl<sub>3</sub> in C<sub>5</sub>H<sub>5</sub>N at room temp.]. The following oxidations with NHAcBr are recorded: *trans*-androsterone to androstanedione (VI) in 58.5% yield; androstanediol to (VI) in 82.5% yield; Me 12(β)-hydroxy- to Me 12-ketocholanate in high yield; Me deoxycholate to Me diketocholanate; deoxycorticosterone to an entirely neutral product, probably Δ<sup>4</sup>-pregnen-21-al-3:20-dione; progesterone is scarcely attacked and cryst. products are not obtained from 21-acetoxy-Δ<sup>4</sup>-pregnene-17(β):20-diol-3-one and substance J. M.p. are corr. (block).

H. W.

**Bile acids and related substances. XXIV. Esters of 3(β)-hydroxy-11-keto- and 3(β):11(a)-dihydroxy-cholanic acid.** J. Press, P. Grandjean, and T. Reichstein (*Helv. Chim. Acta*, 1943, 26, 598—606).—Me 3(β)-acetoxy-Δ<sup>11</sup>-cholenate (I) is transformed by NHAcBr in aq. COMe<sub>2</sub> at 20° into a difficultly separable mixture converted by oxidation (CrO<sub>3</sub>), debromination (Zn dust), and chromatography (Al<sub>2</sub>O<sub>3</sub>) into (I), Me 11-keto-3(β)-acetoxycholanate (II), m.p. 173—174°, [α]<sub>D</sub><sup>17</sup> +56.4° ± 2° in COMe<sub>2</sub>, and Me 12-keto-3(β)-acetoxy-Δ<sup>9</sup>-cholenate (III), m.p. 192—193°, [α]<sub>D</sub><sup>20</sup> +73.9° ± 4° in COMe<sub>2</sub>. (III) is closely similar to Me 12-keto-3(β)-acetoxycholanate, m.p. 184—186°, [α]<sub>D</sub><sup>19</sup> +77.9° ± 2° in COMe<sub>2</sub>, from which it is best differentiated by its ultra-violet absorption spectrum. (II) is rather more readily obtained by cautious hydrogenation (AcOH containing a little PtO<sub>2</sub>) of Me 3:11-diketocholanate and separation of the products by digitonin, thus giving much Me 3(β)-hydroxy-11-ketocholanate (IV), m.p. 152—153°, [α]<sub>D</sub><sup>21</sup> +39.4° ± 2° in COMe<sub>2</sub>, with little 3(a)-OH-ester. (IV) is acetylated to (II). Energetic reduction of (II) leads to Me 11(a)-hydroxy-3(β)-acetoxycholanate, m.p. 139—140°, [α]<sub>D</sub><sup>20</sup> +50.0° ± 2° in COMe<sub>2</sub>, oxidised to (II). (I) and Br in CHCl<sub>3</sub> give Me 11:12-dibromo-3(β)-acetoxycholanate, m.p. 172—175°. M.p. are corr. (block); limit of error ± 2°.

H. W.

**Bile acids and related substances. XXI. 12-Keto-3(a)-acetoxy- and 3(a)-hydroxy-Δ<sup>9</sup>-cholenic acid.** E. Seebeck and T. Reichstein (*Helv. Chim. Acta*, 1943, 26, 536—562).—The greatest difficulty in the prep. and investigation of 3(a)-hydroxy-Δ<sup>9</sup>-cholenic acid (I) is its isomorphism with 3(a)-hydroxy-Δ<sup>11</sup>-cholenic and lithocholenic acid. These acids are very difficult to separate and characterise, the only certain method being by chromatography after acetylation, methylation, and treatment with BzO<sub>2</sub>H. An approx. determination of each component in a mixture may thus be effected. The (I) of Chakravorty *et al.* (A., 1940, II, 179) is shown to be non-homogeneous. 12-Keto-3(a)-acetoxycholanate is brominated according to Longwell *et al.* (*ibid.*, 95), and the product is separated with difficulty into 11(β)-bromo-12-keto-3(a)-acetoxycholanate (II), m.p. 220—222°, [α]<sub>D</sub><sup>17</sup> +39.2° ± 2° in COMe<sub>2</sub>, and the corresponding 11(a)-acid (III), m.p. 179—182°. (II) and (III) with CH<sub>2</sub>N<sub>2</sub> in Et<sub>2</sub>O afford Me esters (IV), m.p. 160—161°, [α]<sub>D</sub><sup>18</sup> +37.5° ± 1° in CHCl<sub>3</sub>, and (V), forms, m.p. 100—101°, and 159—161° [α]<sub>D</sub><sup>19</sup> +47.3° ± 2° in CHCl<sub>3</sub>, respectively. The isolation of (II) is not always reproducible and the esters can be obtained directly from the crude brominated product whereby (V) is copiously but (IV) sparingly secured. (VI) is readily transformed by boiling C<sub>5</sub>H<sub>5</sub>N into Me 12-keto-3(a)-acetoxy-Δ<sup>9</sup>-cholenate (VI), m.p. 145—147°, [α]<sub>D</sub><sup>20</sup> +110.8° ± 2° in CHCl<sub>3</sub>, [α]<sub>D</sub><sup>18</sup> +101.4° ± 1.5° in COMe<sub>2</sub>, the homogeneity of which is best established by its ultra-violet absorption spectrum; (V) under similar conditions is little affected by C<sub>5</sub>H<sub>5</sub>N but passes into (VI) in boiling collidine. (VI) with 1% HCl-MeOH at 18° gives Me 3(a)-hydroxy-12-keto-Δ<sup>9</sup>-cholenate (VII), m.p. 115—116°, [α]<sub>D</sub><sup>14</sup> +93.2° ± 2° in COMe<sub>2</sub>, hydrolysed by alkali to the acid, m.p. 173—174°, [α]<sub>D</sub><sup>16</sup> +96.1° ± 5° in COMe<sub>2</sub> [semicarbazone, m.p. 270° (decomp.)], which is acetylated by boiling AcOH-Ac<sub>2</sub>O to 12-keto-3-acetoxy-Δ<sup>9</sup>-cholenic acid, m.p. 205—206°, [α]<sub>D</sub><sup>18</sup> +99.2° ± 2° in COMe<sub>2</sub> (cf. Longwell *et al.*, *loc. cit.*). (VII) is oxidised by CrO<sub>3</sub> in AcOH to Me 3:12-diketo-Δ<sup>9</sup>-cholenate, m.p. 131—132°, [α]<sub>D</sub><sup>19</sup> +71.6° ± 2° in COMe<sub>2</sub>. Non-homogeneous (VI) is reduced by N<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>O and NaOEt-EtOH at 180° to a mixture (VIII), m.p. 132—134°, [α]<sub>D</sub><sup>13</sup> +62.6° ± 2° in COMe<sub>2</sub>, of Me 3(a)-acetoxy-Δ<sup>9</sup>- (IX), and -Δ<sup>11</sup>-cholenate (X) and Me

acetyl-lithocholate (XI). (VIII) and excess of BzO<sub>2</sub>H in CHCl<sub>3</sub> give Me 9:11-oxido-3(a)-acetoxycholanate (XII), m.p. 121—122°, [α]<sub>D</sub><sup>13</sup> +44.1° ± 2° in COMe<sub>2</sub> (main product), and Me 11:12-oxido-3(a)-acetoxycholanate, m.p. 140—142°. Similar reduction of pure (VI) leads to a mixture (XIII) containing (IX) and (X) but apparently no (XI). Hydrogenation (Raney Ni in MeOH) of (XII) gives inconclusive results but (XI) is obtained by treatment of (XIII) with H<sub>2</sub>-PtO<sub>2</sub> in AcOH. Me 11(a)-hydroxy-3(a)-acetoxycholanate, m.p. 146—148°, is transformed by SOCl<sub>2</sub> or POCl<sub>3</sub> in anhyd. C<sub>5</sub>H<sub>5</sub>N at room temp. into (IX), m.p. 138—140°, [α]<sub>D</sub><sup>14</sup> +62.9° ± 2° in COMe<sub>2</sub>, converted by BzO<sub>2</sub>H in CHCl<sub>3</sub> into (XII) and hydrolysed by KOH in boiling EtOH to (I), m.p. 190—192°, [α]<sub>D</sub><sup>13.5</sup> +46.9° ± 2° in abs. EtOH (acetate, m.p. 176—179°, [α]<sub>D</sub><sup>13</sup> +60° ± 2° in COMe<sub>2</sub>; Me ester, m.p. 105—107°, [α]<sub>D</sub><sup>13.5</sup> +45.3° ± 2° in COMe<sub>2</sub>) (Me lithocholate has [α]<sub>D</sub><sup>13</sup> +32.8° ± 2° in COMe<sub>2</sub>). (IX) is oxidised by CrO<sub>3</sub> in AcOH at 40° to (VI). Non-cryst. materials are obtained from (XII) and boiling HCl-AcOH followed by methylation and acetylation of the crude product. M.p. are corr. (block); limit of error ~ ± 2°.

H. W.

**Bile acids and related substances. XXV. Esters of 3-keto- and 3(a)- and 3(β)-hydroxy-Δ<sup>11</sup>-ætiocolenic acid.** A. Lardon and T. Reichstein (*Helv. Chim. Acta*, 1943, 26, 607—619).—3(a):12(β)-Dihydroxyætiocolenic acid is converted by successive treatments with CH<sub>2</sub>N<sub>2</sub> and Ac<sub>2</sub>O-C<sub>5</sub>H<sub>5</sub>N at 100° into Me 3(a):12(β)-diacetoxy-ætiocolenate, m.p. 149—150°, [α]<sub>D</sub><sup>25</sup> +149.8° ± 1.5° in COMe<sub>2</sub>. This is converted by HCl-MeOH at 18° into Me 3(a)-hydroxy-12(β)-acetoxyætiocolenate, m.p. 141—142°, [α]<sub>D</sub><sup>17</sup> +143.6° ± 3° in COMe<sub>2</sub>, oxidised by CrO<sub>3</sub> in AcOH at 18° to Me 3-keto-12(β)-acetoxyætiocolenate (I), m.p. 95—96°, [α]<sub>D</sub><sup>16</sup> +138° ± 2° in COMe<sub>2</sub>. Alkaline hydrolysis of (I) followed by re-esterification yields the 12(β)-OH-ester (II), m.p. 144—145°, [α]<sub>D</sub><sup>16</sup> +105.9° ± 2° in COMe<sub>2</sub>. BzCl and abs. C<sub>5</sub>H<sub>5</sub>N in C<sub>6</sub>H<sub>6</sub> at 20° followed by MeOH-C<sub>5</sub>H<sub>5</sub>N and AcOH convert (II) into Me 3-keto-12(β)-benzoyloxycholanate (III), unstable transparent granules, m.p. 148—150°, or stable granules or prisms, m.p. 197—198°, [α]<sub>D</sub><sup>19</sup> +117.9° ± 3° in COMe<sub>2</sub>; in an individual experiment in which the treatment with AcOH was omitted the product appeared to be the corresponding Me<sub>2</sub> acetal, m.p. 115—117°, [α]<sub>D</sub><sup>16</sup> +105.7° ± 2° in COMe<sub>2</sub>, converted by boiling aq. AcOH into (III). (III) at 330—340°/12 mm. and later at 380—400°/12 mm. gives Me 3-keto-Δ<sup>11</sup>-ætiocolenate (IV), m.p. 133—135°, [α]<sub>D</sub><sup>16</sup> +79.1° ± 2° in COMe<sub>2</sub>, hydrogenated (PtO<sub>2</sub> in AcOH) to Me 3-ketoætiocolenate and reduced [Al(OPr)<sub>3</sub> in Pr<sup>β</sup>OH] to Me 3(a)- (V), m.p. 122—124°, [α]<sub>D</sub><sup>16</sup> +77.7° ± 2.5° in COMe<sub>2</sub>, and Me 3(β)-hydroxy-Δ<sup>11</sup>-ætiocolenate (VI), m.p. 131—133°, [α]<sub>D</sub><sup>16</sup> +70.7° ± 2° in COMe<sub>2</sub>. The 1:1 compound of (V) and (VI) has m.p. 142—143°. (V) or (VI) is oxidised by CrO<sub>3</sub> in AcOH to (IV). Me 3(a)- and 3(β)-acetoxy-Δ<sup>11</sup>-ætiocolenate have m.p. 99—100°, [α]<sub>D</sub><sup>17</sup> +87.7° ± 2° in COMe<sub>2</sub>, and m.p. 70—72°, [α]<sub>D</sub><sup>21</sup> +62.5° ± 2° in COMe<sub>2</sub>, respectively. M.p. are corr. (block).

H. W.

**Bile acids and related substances. XXIII. Esters of 3:11-diketo-, 3(a)-hydroxy-11-keto- and 3(a):11(a)-dihydroxy-cholanic acid.** A. Lardon and T. Reichstein [with, in part, P. Grandjean] (*Helv. Chim. Acta*, 1943, 26, 586—598).—Me 3-keto-Δ<sup>11</sup>-cholenate (I) in COMe<sub>2</sub> is treated with aq. NHAcBr at room temp. and the crude product is oxidised (CrO<sub>3</sub> in AcOH), debrominated (Zn dust in AcOH), and separated (Al<sub>2</sub>O<sub>3</sub>) into unchanged (I), Me 3:11-diketocholanate (II), m.p. 82—84°, [α]<sub>D</sub><sup>17</sup> +61.7° ± 2° in COMe<sub>2</sub>, and Me 3:12-diketo-Δ<sup>9</sup>-cholenate (III), m.p. 130—131°, [α]<sub>D</sub><sup>15</sup> +71.7° ± 2° in COMe<sub>2</sub>. The brominated product from (I) contains Me 11:12-dibromo-3-ketocholanate, m.p. 136—138°, and (probably) Me 11(a):12(a)-oxido-3-ketocholanate, m.p. 122—124°. Similar bromination, oxidation, and debromination of Me 3-acetoxy-Δ<sup>11</sup>-cholenate leads to Me 11-keto-3(a)-acetoxycholanate (IV), m.p. 132—133°, [α]<sub>D</sub><sup>17</sup> +67.1° ± 2° in COMe<sub>2</sub>, and Me 12-keto-3(a)-acetoxy-Δ<sup>9</sup>-cholenate (V), m.p. 149—150°, [α]<sub>D</sub><sup>17</sup> +102.5° ± 1.5° in COMe<sub>2</sub>. (IV) is converted by alkaline hydrolysis, esterification, and oxidation into (II) and (V) similarly into (III). (IV) is hydrogenated (PtO<sub>2</sub> in AcOH at 20°) to Me 11(a)-hydroxy-3(a)-acetoxycholanate (VI), m.p. 146—148°, [α]<sub>D</sub><sup>17</sup> +70.7° ± 2° in COMe<sub>2</sub>, reoxidised to (IV). Acid hydrolysis followed by methylation and reacetylation of (VI) gives a product, m.p. 135—137°, [α]<sub>D</sub><sup>15</sup> +59.7° ± 2° in COMe<sub>2</sub>, which, although apparently homogeneous, is probably a mixture of Me 3(a)-acetoxy-Δ<sup>9</sup>- and -Δ<sup>11</sup>-cholenate. M.p. are corr. (block).

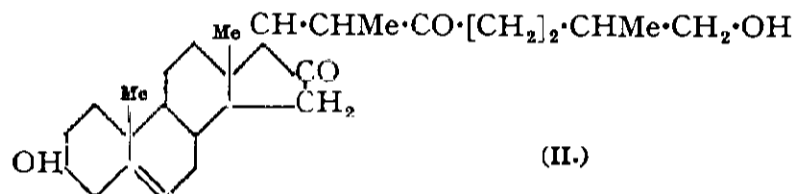
H. W.

**Preparation of homologues of 3-hydroxy-12-ketocholanic acid.** E. Schwenk, B. Riegel, R. B. Moffett, and (Miss) E. Stahl (*J. Amer. Chem. Soc.*, 1943, 65, 549—551).—Deoxycholic acid 3-H succinate (prep. in C<sub>5</sub>H<sub>5</sub>N), m.p. 231—232°, [α]<sub>D</sub> +51.5° (Me<sub>2</sub> ester, m.p. 98—100°), with CrO<sub>3</sub>-AcOH at room temp. and then boiling aq. alkali gives 3-hydroxy-12-ketocholanic acid, [α]<sub>D</sub> +86.6° (lit. +110°) (3-H succinate, m.p. 242—244°; 3-acetate Me ester, m.p. 148.5—150°). Similarly, nordeoxycholic acid 3-H succinate, m.p. 241—242°, [α]<sub>D</sub> +54.8°, gives 3-hydroxy-12-ketonorcholanic acid 3-H succinate (77.3%), m.p. 257—258°, and thence the free acid, m.p. 250—251°, [α]<sub>D</sub> +69.7° (3-acetate, m.p. 207.8—209.5°, [α]<sub>D</sub> +99.7°), the semicarbazone, decomp. ~250—275°, of which with NaOEt-EtOH at 180—200° gives norlithocholic acid (>44%), m.p. 183—

183.5° (cf. lit.). *Bisnordeoxycholic acid 3-H succinate*, m.p. 234—235°,  $[\alpha]_D^{25} + 33.9^\circ$ , gives *3-hydroxy-12-ketobisnorcholanolic acid*, m.p. 298—299°,  $[\alpha]_D^{25} + 84.6^\circ$  [3-acetate, m.p. 246—247°,  $[\alpha]_D^{25} + 65.9^\circ$ ; semicarbazone, decomp.  $\sim 210$ —230° (gas)], by way of its 3-H succinate, m.p. 252—254°. Crude 3-hydroxy-12-keto $\alpha$ -deoxycholic acid 3-H succinate, m.p. 161—169°, gives *3-hydroxy-12-keto $\alpha$ -tiocholanolic acid*, m.p. 213—215°,  $[\alpha]_D^{25} + 127.2^\circ$  (3-acetate, m.p. 205—206°).  $[\alpha]$  are in dioxan. M.p. are corr. R. S. C.

**Authentic  $\Delta^1$ -androsten-17-ol-3-one, an isomeride of testosterone.** A. Butenandt and H. Dannenberg (*Ber.*, 1940, **73**, [B], 206—208).—2-Bromoandrostan-17-ol-3-one acetate passes without isomerisation in boiling collidine into  $\Delta^1$ -androsten-17-ol-3-one acetate (I), m.p. 122°,  $[\alpha]_D^{25} + 47.2^\circ$  in EtOH [oxime (+1H<sub>2</sub>O), m.p. 112° (decomp.), softens at 98°]. (I) is hydrolysed (KOH in boiling MeOH) to  $\Delta^1$ -androsten-17-ol-3-one (II), m.p. 150°,  $[\alpha]_D^{18} + 53.3^\circ$  in EtOH, the constitution of which is established by its absorption spectrum, and by its oxidation (CrO<sub>3</sub> in AcOH) to  $\Delta^1$ -androsterone-3:17-dione, m.p. 138—139°,  $[\alpha]_D^{25} + 144.0^\circ$  in EtOH, which is reduced (Na-Pr <sup>$\beta$</sup> OH) to isoandrostan-3:17-diol, m.p. 163—164° (diacetate, m.p. 122°). According to the Fussgänger test (II) belongs to the most active class of compounds of the androsterone series whereas in the other tests it is much inferior to testosterone. The pronounced oestrogenic activity previously ascribed to the  $\Delta^1$ -unsaturated compounds of the androsterone series appears to be confined to the isomeric "hetero- $\Delta^1$ -compounds." H. W.

**Sterols. CLIII. Sapogenins. LXV. Kryptogenin, a new type of sapogenin from *Beth root*.** R. E. Marker, R. B. Wagner, D. P. J. Goldsmith, P. R. Ulshafer, and C. H. Ruof (*J. Amer. Chem. Soc.*, 1943, **65**, 739).—Roots of *Trillium erectum* contain about equal amounts of diosgenin (I) (A., 1941, III, 62) and *kryptogenin* (II), C<sub>27</sub>H<sub>42</sub>O<sub>4</sub>, m.p. 187—189°. With Na-Pr <sup>$\beta$</sup> OH, (II) gives (I) (isolated



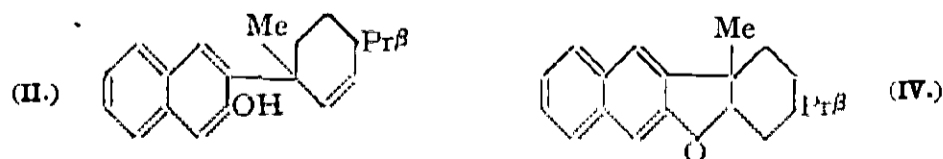
as acetate) and with H<sub>2</sub>-PtO<sub>2</sub> in Et<sub>2</sub>O + AcOH (a little) gives the 5:6-H<sub>2</sub>-derivative, m.p. 169—171°, which with CrO<sub>3</sub>-AcOH gives 3-dehydrotigogenoic acid. The structure shown is assigned to (II). No details are given. R. S. C.

## V.—TERPENES AND TRITERPENOID SAPOGENINS.

**Inversion of menthone with hydrogen chloride in benzene.** A. Weissberger and D. S. Thomas, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 402—403).—Inversion of *l*-menthone (I) by HCl in C<sub>6</sub>H<sub>6</sub> at 20.0  $\pm$  0.1° is shown kinetically to proceed by way of a complex, (I) + 2HCl. R. S. C.

**Synthetic production of camphor from pinene. IV. Oxidation of borneols to camphor.** B. G. S. Acharya, R. C. Shah, and T. S. Wheeler (*J. Univ. Bombay*, 1943, **11**, A, Part 5, 113—115).—Methods of oxidising borneol to camphor are reviewed. 96% of camphor is obtained from isoborneol with 35% HNO<sub>3</sub>—50% H<sub>2</sub>SO<sub>4</sub> at 75—85°. A. L.

**Reaction of  $\beta$ -naphthol with dienes.** J. C. Salfeld (*Ber.*, 1940, **73**, [B], 376—385).— $\beta$ -C<sub>10</sub>H<sub>7</sub>OH (I) and  $\alpha$ -phellandrene at 130° give an adduct (II), C<sub>20</sub>H<sub>24</sub>O, m.p. 139—140° (p-nitrobenzoate, m.p. 164—165°). (I) and Me sorbate at 180° yield the lactone, 2:3-C<sub>10</sub>H<sub>6</sub>·CH·CH<sub>2</sub>·CH:CHMe (III), m.p. 102—103°, which with Me<sub>2</sub>SO<sub>4</sub>-MeOH-aq. KOH gives the corresponding OMe-acid, m.p. 114—115°, and with Br-AcOH-Et<sub>2</sub>O affords the dibromide, m.p.



222—224° [Zn-EtOH gives (III)]. With  $\Delta^1$ : $\alpha$ -cyclohexadiene, (I) affords an adduct, C<sub>18</sub>H<sub>16</sub>O, b.p. 175—178°/1 mm. (picrate, m.p. 121°; p-nitrobenzoate, m.p. 171—172°). (II) with Se at 275°, or with HCl-MeOH, gives the compound (IV), m.p. 105—106° (picrate, m.p. 126—127°), also obtained in small amount from (I),  $\alpha$ -phellandrene, and ZnCl<sub>2</sub>-AcOH at 0° (2 days), then at room temp. (1 day), and then at 100° (bath) (1 hr.). Br-AcOH converts (IV) into a Br<sub>1</sub>-derivative, m.p. 130—132°. (II) is hydrogenated (Pd-C; EtOH; 1 mol. of H<sub>2</sub>) to a H<sub>2</sub>- (p-nitrobenzoate, m.p. 135—136°) or (3 mols. of H<sub>2</sub>) H<sub>8</sub>-derivative (p-nitrobenzoate, m.p. 177—179°). The p-nitrobenzoate of (II) and BzO<sub>2</sub>H in CHCl<sub>3</sub> give an oxide, C<sub>27</sub>H<sub>27</sub>O<sub>5</sub>N, m.p. 179—180°, hydrolysed by KOH-MeOH to a compound, C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>, m.p. 153—154° (non-cryst. acetate). (III) similarly affords an oxide, C<sub>16</sub>H<sub>14</sub>O<sub>3</sub>, m.p. 144—145°. A. T. P.

**Triterpenediols. VI. Faradiol and arnidiol.** J. Zimmermann (*Helv. Chim. Acta*, 1943, **26**, 642—647; cf. A., 1941, III, 714).—The isolation of faradiol (I), m.p. 236—237°,  $[\alpha]_D^{25} + 44.5^\circ$  in CHCl<sub>3</sub> (diacetate, m.p. 163—167°,  $[\alpha]_D^{25} + 55.5^\circ$  in CHCl<sub>3</sub>), and arnidiol (II), m.p. 257°,  $[\alpha]_D^{25} + 82.7^\circ$  in CHCl<sub>3</sub> (diacetate, m.p. 193°,  $[\alpha]_D^{25} + 80.4^\circ$  in CHCl<sub>3</sub>), from arnica, sunflower, and coltsfoot is described. The diketone obtained by oxidation of (I) has m.p. 242° and that from (II), m.p. 254° (dioxime, m.p. 268°). The diacetates of dihydrofaradiol and -arnidiol have m.p. 196° and 210°, respectively. Dihydrofaradiol and -arnidiol give the same diketone, m.p. 182° (dioxime, m.p. 253—254°). (I) is distinguished from (II) by the position of the double linking and the steric position of the OH groups in the mol. (I) diacetate is isomerised by 90% HCO<sub>2</sub>H to a substance, C<sub>34</sub>H<sub>54</sub>O<sub>4</sub>, m.p. 255°,  $[\alpha]_D^{25} + 89.6^\circ$ . Triterpenes could not be obtained from the disc florets, fruits, receptacle, stalk, and upper stem, pericarp, or seeds of sunflower but only from the ray florets. The same sitosterol glucoside is present in all parts of the plant; it is characterised by its tetra-acetate, m.p. 168°. H. W.

**Carotenoids from the blossoms of the chrysanthemum. Chrysanthemaxanthin.**—See A., 1943, III, 615.

**Cardanol derivatives.**—See B., 1943, II, 212.

## VI.—HETEROCYCLIC.

**Condensation of 2-furylacetic acid with o-nitrobenzaldehyde.** E. D. Amstutz and E. R. Spitzmiller (*J. Amer. Chem. Soc.*, 1943, **65**, 367—369).—K 2-furylacetic acid, o-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO, and Ac<sub>2</sub>O at, best (100.7% of crude ketone), 75° give cis- (I) (42.6%), m.p. 192—192.4° (corr.), and trans-o-nitro- $\alpha$ -2-furylcinnamic acid (II) (23.2%), m.p. 137.6—138.2° (corr.), configurations referring to Ph and furyl. With a trace of I in PhNO<sub>2</sub> at 210°, (II) gives  $\leq 58\%$  of (I). Decarboxylation of (I) and (II) gives cis- (III), b.p. 152—154°/3 mm., and trans- $\beta$ -o-furylstyrene (IV) (15%), m.p. 92.8—93.6° (corr.), respectively. In quinoline at 230°, (III) gives a trace of crystals, possibly (IV). With FeSO<sub>4</sub>-aq. NH<sub>3</sub>, (II) gives o-amino- $\alpha$ -2-furylcinnamic acid (78%), m.p. 156°, which resists "Pschorr" ring-closure. R. S. C.

**Tetrahydropyranyl amino-alcohols.** G. H. Harnest and A. Burger (*J. Amer. Chem. Soc.*, 1943, **65**, 370—372).—(CHMeCl-CH<sub>2</sub>)<sub>2</sub>O does not react with CHNa(CO<sub>2</sub>Et)<sub>2</sub> (I) or NaI-COMe<sub>2</sub>. Tetrahydropyran-4-carboxylic acid is obtained in 52% yield by successive condensation of (Cl-CH<sub>2</sub>)<sub>2</sub>O with (I), hydrolysis (KOH-aq. EtOH), and decarboxylation (175—185°). With SOCl<sub>2</sub> it gives the acid chloride, b.p. 93—95°/21 mm., and thence (CH<sub>2</sub>N<sub>2</sub>-Et<sub>2</sub>O) 4-diazo-, m.p. 42—45° (decomp.), and (48% aq. HBr-Et<sub>2</sub>O at 0°) 4-bromo-acetyltetrahydropyran, lachrymatory, m.p. 50—53°. With NHR<sub>2</sub> (2.5 mols.) in Et<sub>2</sub>O at room temp., this (1 mol.) gives 4-diethylamino-, m.p. 152—155°, 4-piperidino-, m.p. 177—179°, and 4-morpholino-acetyltetrahydropyran hydrochloride, m.p. 214—219°, reduced by H<sub>2</sub>-PtO<sub>2</sub> in EtOH to 4- $\alpha$ -hydroxy- $\beta$ -diethylamino-, m.p. 140.5—142°, -piperidino- (II), m.p. 208—210° (acetate hydrochloride, m.p. 211—213°), and -morpholino-ethyltetrahydropyran hydrochloride, m.p. 213—216° (acetate hydrochloride, m.p. 223—225°). NH<sub>3</sub>-Et<sub>2</sub>O and (I) give the amide, dehydrated by P<sub>2</sub>O<sub>5</sub> at 180—280°/20 mm. to 4-cyanotetrahydropyran, b.p. 100—102°/25 mm. Et 4-cyanotetrahydropyran-4-carboxylate has b.p. 130—134°/23 mm. (cf. lit.). (II) is analgesic. Some tetrahydropyranylhydantoins are mild anticonvulsants, but not hypnotic. M.p. are corr. R. S. C.

**Vitamin-E. XL. Synthesis and properties of 4-hydroxy-3:4:5-trimethyl-1-isopropylcoumaran.** L. I. Smith and J. A. King (*J. Amer. Chem. Soc.*, 1943, **65**, 441—444; cf. A., 1941, II, 326).—Adding Na and then COMePr <sup>$\beta$</sup>  to Pr <sup>$\beta$</sup> CO<sub>2</sub>Et gives CH<sub>2</sub>(COPr <sup>$\beta$</sup> )<sub>2</sub> (28%), b.p. 62—63°/3 mm., which with NaOEt-EtOH and then O:C<sub>6</sub>HMe<sub>3</sub>:O at  $< 25^\circ$  (later 0°) gives  $\delta$ -2:5-dihydroxy-3:4:6-trimethylphenyl- $\beta$ - $\gamma$ -dimethyl-n-heptane- $\gamma$ -dione (76%), m.p. 135—135.5°. With a drop of H<sub>2</sub>SO<sub>4</sub> in AcOH this gives  $\alpha$ -5-acetoxy-2-isobutyroxy-3:4:6-trimethylphenyl- $\gamma$ -methylbutan- $\beta$ -one (I), m.p. 113°, or with boiling HCl-EtOH gives 4-hydroxy-3:5:6-trimethyl-1-isopropylbenzofuran, m.p. 118° (acetate, m.p. 69—70°), also obtained similarly from (I), and reduced by H<sub>2</sub>-Raney Ni at 125°/1300 lb. to 4-hydroxy-3:5:6-trimethyl-1-isopropyl-1:2-dihydrobenzofuran (II), m.p. 112° (acetate, m.p. 72—73°). Aq. AuCl<sub>3</sub> or FeCl<sub>3</sub> oxidises (II) to 2:3:5-trimethyl-6- $\beta$ -hydroxyisoamyl-1:4-benzoquinone, an oil, reduction of which by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>-H<sub>2</sub>O-MeOH or boiling Zn-AcOH yields (II) directly, no quinol being obtainable. R. S. C.

**Condensation of  $\alpha$ -substituted acetoacetates with phenols. VI. Condensation of phenols with ethyl acetosuccinate. VII. Condensation of substituted phenols with ethyl acetosuccinate.** R. H. Shah and N. M. Shah (*J. Indian Chem. Soc.*, 1942, **19**, 481—485, 486—488).—VI. CO<sub>2</sub>Et·CHAc·CH<sub>2</sub>·CO<sub>2</sub>Et has been condensed with phenols in the presence of different catalysts. Resorcinol yields (POCl<sub>3</sub> or P<sub>2</sub>O<sub>5</sub>) Et 7-hydroxy-4-methylcoumarin-3-acetate [acetate (I), m.p. 98°; benzoate, m.p. 138° (lit. 127°)], or (AlCl<sub>3</sub>) the free

acid [acetate (II), m.p. 199—200°; benzoate, m.p. 190—191°]. (II) is decarboxylated by Cu-bronze in boiling quinoline. (I) is converted by  $\text{AlCl}_3$  at 120—125° into 7-hydroxy-8-acetyl-4-methylcoumarin-3-acetic acid. Orcinol ( $\text{POCl}_3$  or  $\text{H}_2\text{SO}_4$ ) yields the Et ester, m.p. 206° (lit. 198—200°) (acetate, m.p. 91—92°), of 5-hydroxy-4:7-dimethylcoumarin-3-acetic acid, m.p. 270° (acetate, m.p. 183—184°). Pyrogallol yields (conc.  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ -cooling) 7:8-dihydroxy-4-methylcoumarin-3-acetic acid, m.p. 270° (acetate, m.p. 224—225°), or [ $\text{H}_2\text{SO}_4$  (ice-cooling) or  $\text{POCl}_3$ ] its Et ester, m.p. 206° (lit. 186°) (acetate, m.p. 123—124°). Phloroglucinol yields (80%  $\text{H}_2\text{SO}_4$ ) 5:7-dihydroxy-4-methylcoumarin-3-acetic acid, m.p. >285° (acetate, m.p. 169—170°) or ( $\text{POCl}_3$ ) its Et ester, m.p. 250° (acetate, m.p. 114—115°).  $\alpha$ - and  $\beta$ - $\text{C}_{10}\text{H}_7\text{OH}$  yield respectively 4-methyl- $\alpha$ -, m.p. 253—254° ( $\text{AlCl}_3$ ,  $\text{POCl}_3$ , or 80%  $\text{H}_2\text{SO}_4$ ), or its Et ester, m.p. 141° (lit. 137°), and  $\beta$ -naphthapyrone-3-acetic acid (conc.  $\text{H}_2\text{SO}_4$ ) (Et ester, m.p. 101°). *m*-Cresol yields (conc.  $\text{H}_2\text{SO}_4$ ) Et 4:7-dimethylcoumarin-3-acetate, m.p. 106° (free acid, m.p. 193—194°).

VII. With  $\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , Me  $\beta$ -resorcyate yields (80%  $\text{H}_2\text{SO}_4$ ) Me 7-hydroxy-4-methylcoumarin-6-carboxylate; 2:1:3- $\text{C}_6\text{H}_3\text{Ac}(\text{OH})_2$  yields ( $\text{POCl}_3$ ) Et 7-hydroxy-8-acetyl-4-methylcoumarin-3-acetate, m.p. 167—168° (acetate, m.p. 221—223°), or (80%  $\text{H}_2\text{SO}_4$ ) the free acid, m.p. 262—263°; 2:1:3- $\text{C}_6\text{H}_3\text{Bz}(\text{OH})_2$  yields ( $\text{POCl}_3$ ) Et 7-hydroxy-8-benzoyl-4-methylcoumarin-3-acetate, m.p. 196—197° (acetate, m.p. 177°; free acid, m.p. 255°); 4:1- $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{OH}$  yields (conc.  $\text{H}_2\text{SO}_4$ ) Et 6-chloro-4-methyl-1:2- $\alpha$ -naphthapyrone-3-acetate, m.p. 185—186° (lit. 181—184°), or (80%  $\text{H}_2\text{SO}_4$ ) the free acid, m.p. 276—277° (anilide, m.p. 265—266°); 4:1:3- $\text{C}_6\text{H}_3\text{Cl}(\text{OH})_2$  yields ( $\text{POCl}_3$  or conc.  $\text{H}_2\text{SO}_4$ ) Et 6-chloro-7-hydroxy-4-methylcoumarin-3-acetate (acetate, m.p. 169°; free acid, m.p. 263°), but 4:1:3- $\text{C}_6\text{H}_3\text{Br}(\text{OH})_2$  gives ( $\text{POCl}_3$ ) Et 7-hydroxy-4-methylcoumarin-3-acetate. The effect of substituents on the reaction is discussed.

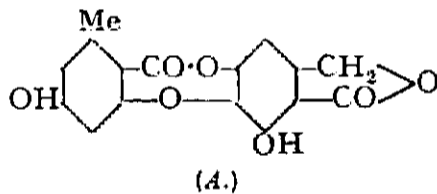
A. LI.

**Constitution of evodionol.** F. N. Lahey (*Univ. Queensland Papers, Dept. Chem.*, 1942, 1, No. 20, 14 pp.).—Evodionol (I) is shown to be 7-hydroxy-5-methoxy-6-acetyl-2:2-dimethyl-1:2-benzopyran (cf. *Univ. Queensland Publication*, 1940, 1, 17). With  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and  $\text{BaCO}_3$  (excess) in boiling EtOH (not other conditions) it gives an oxime, m.p. 89° (green  $\text{FeCl}_3$  colour; brown Cu compound proves the presence of  $\text{OH}\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{N}\cdot\text{OH}$ ), and with  $\text{PhCHO}$  and  $\text{NaOH}$  in ~50% EtOH at room temp. gives a *CHPh*: derivative (II), m.p. 94° (brown  $\text{FeCl}_3$  colour). Dihydroevodionol (the derived chroman) (III) gives similarly an oxime, m.p. 132° (violet  $\text{FeCl}_3$  colour; brown Cu derivative, cf. above), a *CHPh*: (IV), m.p. 118° (red  $\text{FeCl}_3$  colour), and, by boiling  $\text{HNO}_3$ - $\text{H}_2\text{O}$ -EtOH, the 8- $\text{NO}_2$ -derivative, m.p. 158.5°, a 2:4-dinitrophenylhydrazone, m.p. 188°, and acetate, m.p. 84—85°. The Me ether (V) of (I) gives a 2:4-dinitrophenylhydrazone, m.p. 135°, and *CHPh*: derivative (VI), m.p. 114°. The Me ether of (III) gives a 2:4-dinitrophenylhydrazone, m.p. 169°, and *CHPh*: derivative (VII), m.p. 104°; its oxime, m.p. 160—161°, is converted by  $\text{SOCl}_2$  into the amide,  $\text{C}_{15}\text{H}_{21}\text{O}_4\text{N}$ , m.p. 172°, from which, however, only a trace of amine is formed by hydrolysis.  $\text{H}_2$ -PtO<sub>2</sub> at 2 atm. reduces (II) to tetrahydrobenzylidene-evodionol [7-hydroxy-5-methoxy-6- $\beta$ -phenylpropionyl-2:2-dimethylchroman], m.p. 88° (reddish-brown  $\text{FeCl}_3$  colour), hydrolysed by 40% KOH-EtOH at 230—250° to the known 7-hydroxy-5-methoxy-2:2-dimethylchroman, m.p. 103°, and  $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ ; this proves the structure of (I) except for the position of the Ac. Hydrogenation of (VI) gives similarly the known 5:7-dimethoxy-6- $\beta$ -phenylpropionyl-2:2-dimethylchroman, an oil (oxime, m.p. 129.5°), which proves the structure of (I) except for the position of the free OH. The dibasic acid (VIII),  $\text{C}_{15}\text{H}_{18}\text{O}_8$ , obtained from (I) by  $\text{KMnO}_4$ - $\text{COMe}_2$  (*loc. cit.*) is termed evodionic acid; at 140—150° it yields a glassy acid (IX) and small amounts of AcOH, 4:2:6:1- $\text{OH}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{COMe}$  (and thence the Me<sub>3</sub> ether), and 3:5:1- $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{OH}$  (X) [yields  $s\text{-C}_6\text{H}_3(\text{OMe})_3$ ; more formed at 250°; also obtained from (IX)]; (IX) is converted by  $\text{MeOH}\cdot\text{H}_2\text{SO}_4$  into 3:5:4:1-(OMe)<sub>2</sub> $\cdot\text{C}_6\text{H}_2\text{Ac}\cdot\text{O}\cdot\text{COMe}_2\cdot\text{CO}_2\text{Me}$ , m.p. 76°, which is similarly obtained from (VIII) and is synthesised from 4:2:6:1- $\text{OH}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{COMe}$  by  $\text{CMe}_2\text{Br}\cdot\text{CO}_2\text{Me}$  and  $\text{K}_2\text{CO}_3$  in  $\text{COMe}_2$ ; these products confirm the structure of (I). In boiling 25% NaOH, (I), but not (IV), yields  $\text{COMe}_2$ , confirming the 2:2-dimethyl-1:2-benzopyran structure.  $\text{O}_3$  in  $\text{CCl}_4$  converts (V) into 6-hydroxy-2:4-dimethoxy-3-acetylbenzaldehyde, m.p. 76—77° (red  $\text{FeCl}_3$  colour; reduces  $\text{AgNO}_3\text{-NH}_3$ ), converted by  $\text{MeI}\cdot\text{K}_2\text{CO}_3\cdot\text{COMe}_2$  into 2:4:6-trimethoxy-3-acetylbenzaldehyde, m.p. 84° (no  $\text{FeCl}_3$  colour), which with  $\text{KMnO}_4$  in aq.  $\text{COMe}_2$  yields 2:4:6-trimethoxy-3-acetylbenzoic acid, m.p. 149—150°, and thence (heat at 160°) 2:4:6:1- $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{COMe}$ . Interaction of (VIII) with  $\text{KOH}$  is re-interpreted thus: 1:3:2:5-6- $\text{CO}_2\text{H}\cdot\text{C}_6\text{HAc}(\text{OMe})_2\cdot\text{O}\cdot\text{COMe}_2\cdot\text{CO}_2\text{H}$  (VIII)  $\rightarrow$  6:2:4:1-3- $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{O}\cdot\text{C}_6\text{H}(\text{OMe})_2(\text{CO}_2\text{H})_2 \rightarrow$  3:5:2:4:1-(OMe)<sub>2</sub> $\cdot\text{C}_6\text{HBr}_2\cdot\text{O}\cdot\text{COMe}_2\cdot\text{CO}_2\text{H}$ , which with  $\text{Na-Hg}$  yields 3:5:1- $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{O}\cdot\text{COMe}_2\cdot\text{CO}_2\text{H}$  (XI). (XI) is synthesised from (X) by  $\text{CMe}_2\text{Br}\cdot\text{CO}_2\text{Me}$  in  $\text{NaOEt}\cdot\text{EtOH}$  (later hydrolysis by  $\text{KOH}\cdot\text{EtOH}$ ) and, when heated with soda-lime, gives  $s\text{-C}_6\text{H}_3(\text{OMe})_3$  and an oil, possibly 1:3:5- $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{OPr}^i$ , which is also an oil when prepared from (X) by  $\text{Pr}^i\text{I}\cdot\text{K}_2\text{CO}_3\cdot\text{COMe}_2$ . Pyrolysis of 3:5:4:1-(OMe)<sub>2</sub> $\cdot\text{C}_6\text{H}_2\text{Ac}\cdot\text{O}\cdot\text{COMe}_2\cdot\text{CO}_2\text{H}$  also gives a little  $s\text{-C}_6\text{H}_3(\text{OMe})_3$ . Aq.  $\text{KMnO}_4$  oxidises (VII) in  $\text{COMe}_2$  to 5:7-dimethoxy-2:2-dimethyl-

chroman-6-glyoxylic acid, m.p. 169° (decomp.) (2:4-dinitrophenylhydrazone),  $\text{BzOH}$ , and 5:7-dimethoxy-2:2-dimethylchroman, an oil, identified by conversion by  $\text{HCl}\cdot\text{Zn}(\text{CN})_2\cdot\text{Et}_2\text{O}$  into the known 8-CHO derivative (semicarbazone, m.p. 217°; 2:4-dinitrophenylhydrazone, m.p. 242°). Boiling (II) or (IV) in 10%  $\text{H}_2\text{SO}_4$  containing some EtOH gives 5-methoxy-8:8-dimethyl-1:2-pyrano[3:2-g]-flavanone[5-methoxy-2':2'-dimethylpyrano-5':6':6:7-flavanone], m.p. 126°, and its 6:7-[3':4']- $\text{H}_2$ -derivative, m.p. 145—146°, respectively. 5:7-Dihydroxy-6-acetyl-2:2-dimethylchroman (improved prep.) with  $\text{MeI}$  and  $\text{K}_2\text{CO}_3$  in boiling  $\text{COMe}_2$  gives, after 2 hr., 5-hydroxy-7-methoxy-6-acetyl-2:2-dimethylchroman (XII), m.p. 88° (2:4-dinitrophenylhydrazone, m.p. 192°), isomeric with (I), or, after 12 hr., the 5:7-Me<sub>2</sub> ether, m.p. 91°, identical with the Me ether of (III). 2:6-Dibromobenzoquinonechloroimide gives, as expected, a positive test with (XII), but not with (I) or (III). R. S. C.

**Spectrographic study of evodionol and its derivatives.**—See A., 1943, I, 191.

**Chemical constituents of lichens found in Ireland.** *Lecanora parella*, Ach. Constitution of variolaric acid. D. Murphy, J. Keane, and T. J. Nolan (*Sci. Proc. Roy. Dublin Soc.*, 1943, 23, 71—82).—Extraction of the lichen with  $\text{COMe}_2$  gives variolaric acid (I), new formula  $\text{C}_{16}\text{H}_{10}\text{O}_7$ , m.p. 296° (decomp.) after darkening, which gives a purple colour with  $\text{FeCl}_3$ , no colour with  $\text{CaOCl}_2$ , and a blue colour with 2:6-dichloro-*p*-benzoquinonechloroimide. When kept in 10% KOH at room temp. (I) affords ochric acid,  $\text{C}_{16}\text{H}_{12}\text{O}_8$ , m.p. 221—223° with evolution of CO when rapidly heated, and when boiled with 50% aq. KOH it gives a substance (II),  $\text{C}_{14}\text{H}_{14}\text{O}_5$ , m.p. 194—195°, insol. in aq.  $\text{NaHCO}_3$ , and a compound (III),  $\text{C}_{15}\text{H}_{14}\text{O}_7$ , m.p. 188.5° (decomp.) when slowly heated or m.p. 194—196° (decomp.) when rapidly heated. (II) with  $\text{Me}_2\text{SO}_4$  in cold or boiling aq. NaOH gives a Me<sub>1</sub> ether, m.p. 128—129°, whereas  $\text{CH}_2\text{N}_2$  gives a non-cryst. product. With excess of  $\text{CH}_2\text{N}_2$  (III) gives a Me<sub>4</sub> derivative, m.p. 108—109°, whilst with a restricted proportion a Me<sub>1</sub> ester, m.p. 217—218°, results. (II) and (III) do not give cryst. acetates. (I) and  $\text{Ac}_2\text{O}$  containing a little conc.  $\text{H}_2\text{SO}_4$  at room temp. afford a diacetate, m.p. 245—246° after darkening. (I) is transformed by an excess of  $\text{CH}_2\text{N}_2$  in  $\text{COMe}_2$  at room temp. into its Me<sub>2</sub> ether, m.p. 260—261° (blackens), converted by boiling with 10% or 50% aq. KOH into the substance,  $\text{C}_{16}\text{H}_{10}\text{O}_6(\text{OMe})_2$ , m.p. 246° (decomp.); hence (I) contains 2 aromatic OH but no  $\text{CO}_2\text{H}$ . With  $\text{KOH}\cdot\text{MeOH}$  (I) gives a Me<sub>1</sub> ester (IV),  $\text{C}_{16}\text{H}_{11}\text{O}_7(\text{OMe})$ , 1.5 $\text{H}_2\text{O}$ , m.p. 243° (decomp.), converted by  $\text{CH}_2\text{N}_2$  into its Me<sub>3</sub> ether, m.p. 181—182°. When fused with KOH (I) gives orcinol and 3:5:1-(OH)<sub>2</sub> $\cdot\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$ . (IV) is converted by  $\text{Cl}_2$  in  $\text{CHCl}_3\text{-CCl}_4$  at room temp. into Me 2:4-dichloro-*o*-orsellinate, m.p. 115° (corr.). Me 2:6-dichloro-*p*-orsellinate has m.p. 167—169°. Hence (I) is (A). The lichen also contains mannitol. H. W.



converted by  $\text{Cl}_2$  in  $\text{CHCl}_3\text{-CCl}_4$  at room temp. into Me 2:4-dichloro-*o*-orsellinate, m.p. 115° (corr.). Me 2:6-dichloro-*p*-orsellinate has m.p. 167—169°. Hence (I) is (A). The lichen also contains mannitol.

**Pyridines.**—See B., 1943, II, 212.

**Reduction of 3-acetylpyridines.** A. Dornow and H. Machens (*Ber.*, 1940, 73, [B], 355—358).—3-Acetyl-2-methylpyridine (I) and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  at 125° give the hydrazone, which with a little KOH at 150° gives 2-methyl-3-ethylpyridine, b.p. 67—69°/14 mm. (picrate, m.p. 140—141°; methiodide, m.p. 136°), also obtained by Clemmensen reduction of (I). Similarly prepared (Wolff-Kishner) is 2:6-dimethyl-3-ethylpyridine (II), b.p. 75°/13 mm. (picrate, m.p. 122°). Et 2:6-dimethylpyridine-3-carboxylate and boiling  $\text{EtOAc}\cdot\text{NaOEt}$  (free from EtOH) give after hydrolysis by 10% HCl 3-acetyl-2:6-dimethylpyridine (III), reduced to (II). Hydrogenation ( $\text{PtO}_2\text{-H}_2\text{O}$ ) of (III) gives 2:6-dimethyl-3- $\alpha$ -hydroxyethylpyridine (IV), m.p. 69°, also obtained by Clemmensen reduction of (III), or similarly from the corresponding 3- $\text{CH}_2\text{Br}\cdot\text{CO}$  compound after treatment with  $\text{AcOH}\cdot\text{KOAc}$ . (IV) and  $\text{CrO}_3\cdot\text{AcOH}$  give (III). 2-Methyl-3- $\alpha$ -hydroxyethylpyridine has b.p. 142°/12 mm. A. T. P.

**3:4-Substituted pyridines.** II.  $\beta$ -4-Pyridylpropionic acid. J. R. Stevens and R. H. Beutel (*J. Amer. Chem. Soc.*, 1943, 65, 449—451; cf. A., 1942, II, 328).— $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$  (I) with  $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  and piperidine (II) in warm MeOH gives Et 2:6-dihydroxy-3-cyanopyridine-4-carboxylate, softens 120°, liquid at 150°, isolated as piperidine salt (36%), m.p. 180—181°; with  $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ , and (II) in boiling MeOH it gives Et 2:6-dihydroxy-3-cyano-4-pyridylacetate (31.5%), m.p. 239°.  $\text{CO}_2\text{Et}\cdot[\text{CH}_2]_2\cdot\text{COCl}$  and  $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$  in  $\text{C}_6\text{H}_6$  give Et<sub>2</sub>  $\beta$ -keto- $\alpha$ -acetyladipeate (18.4%), b.p. 65—76°/5  $\times 10^{-3}$ — $10^{-4}$  mm., converted by  $\text{NH}_3\cdot\text{Et}_2\text{O}$  at 0° into Et<sub>2</sub>  $\beta$ -ketoadipate (III) (60%), b.p. 65—70°/10<sup>-3</sup> mm. With  $\text{NHPh}\cdot\text{NH}_2$  at 100°, (III) gives 1-phenyl-3- $\beta$ -carbethoxyethylpyrazolone (86%), m.p. 107.5°, and with (I) and (II) in EtOH at 85° gives Et  $\beta$ -2:6-dihydroxy-3-cyano-4-pyridylpropionate (36.5%), m.p. 247°, hydrolysed by conc. HCl at 150° to  $\beta$ -2:6-dihydroxy-4-pyridylpropionic acid, m.p. 268—269°. With  $\text{POCl}_3$  at 175° this gives  $\beta$ -2:6-dichloro-4-pyridyl- (57%), m.p. 127°, sublimes 115°/10<sup>-3</sup> mm., and thence ( $\text{H}_2\text{-PdCl}_2\text{-C}$ ; MeOH; 30 lb.)  $\beta$ -4-pyridyl-propionic

acid (77%), m.p. 208°.  $\text{OEt} \cdot [\text{CH}_2]_2 \cdot \text{Br}$ , (III), and  $\text{NaOEt} \cdot \text{EtOH}$  give *Et*<sub>2</sub>  $\beta$ -keto- $\alpha$ - $\beta'$ -ethoxyethyladipate (20%), b.p. 90°/5  $\times 10^{-4}$  mm., which could not be condensed with (I). R. S. C.

**Synthesis of pyridinium ethanols. IV. Syntheses with carbethoxymethylpyridinium bromide.** F. Krohnke (*Ber.*, 1940, 73, [B], 310—312; cf. A., 1939, II, 104).— $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{NC}_5\text{H}_5\text{Br}$  (I) and *m*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$  in aq.  $\text{NaOH} \cdot \text{EtOH}$  at 0° give  $\beta$ -hydroxy- $\alpha$ -carbethoxy- $\beta$ -*m*-nitrophenylethylpyridinium betaine, *m*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{CO}_2^-) \cdot \text{N}^+\text{C}_5\text{H}_5$ , m.p. 157° (decomp.); the *o*- $\text{C}_6\text{H}_4\text{Cl}$  analogue decomposes at 145—147° (*picrate*, m.p. 119—120°). (I) and 2:5:1- $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{CHO}$  in aq.  $\text{NaOH} \cdot \text{EtOH}$  at 0° afford  $\beta$ -hydroxy- $\alpha$ -carbethoxy- $\beta$ -2:5-dichlorophenylethylpyridinium bromide, m.p. 148° (decomp.), converted by aq.  $\text{NaOH}$  at room temp. into the corresponding betaine, m.p. 140° (decomp.). (I) and aq.  $\text{NaOH} \cdot \text{EtOH}$  at 0° give a 1:1 compound, m.p. (vac.) 110°, of  $\text{C}_5\text{H}_5\text{N}^+ \cdot \text{CH}_2 \cdot \text{CO}_2^-$  and  $\text{NaBr}$ . A 1:1 compound, m.p. 158—159°, of  $\text{NHPH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NC}_5\text{H}_5\text{Br}$  (A., 1939, II, 208) and *m*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$  is prepared in  $\text{EtOH} \cdot \text{N} \cdot \text{NaOH}$  at 0°. A. T. P.

**Action of dipyridinium radicals on para-hydrogen.**—See A., 1943, I, 204.

**Reduction of quinoline and substituted quinolines in liquid ammonia.** C. M. Knowles and G. W. Watt (*J. Amer. Chem. Soc.*, 1943, 65, 410—412).—Passing  $\text{H}_2$  into quinoline, 5-nitro- (I) or -amino-, or 8-amino-quinoline in  $\text{NH}_3$  containing an excess of  $\text{NH}_4\text{Br}$  at -33.5° gives, without development of colour, 1:4-dihydroquinoline (II) [isolated as the dimeride, m.p. >80° (decomp.)], of the  $\text{Ac}_2$  derivative, the trimeride, m.p. >157° (decomp.), of 5- (III), or the dimeride, m.p. >125° (decomp.), of 8-amino-1:4-dihydroquinoline (IV), respectively. Reduction by  $\text{Na}$  in  $\text{NH}_3$  gives the same products more rapidly, but colours develop prior to the blue due to  $\text{Na}$ ; however, products were isolated as the dimeride, m.p. >100° (decomp.), of the benzoate of (II), the *Et*<sub>4</sub> derivative, m.p. >160° (decomp.), of (III) [from (I)], and the *Bz*<sub>3</sub> derivative, m.p. >148° (decomp.), of (IV); the *Bz*<sub>3</sub> derivative, m.p. >95° (decomp.), of (III) is also used for isolation.  $\text{Na}$  reduces 8-nitroquinoline in  $\text{NH}_3$ , yielding (IV), which is isolated as the *Et*<sub>4</sub> derivative, m.p. >155° (decomp.), but  $\text{H}_2$  gives a gum unless  $\text{Et}_2\text{O}$  is used as diluent. Cessation of reduction at the  $\text{H}_2$ -stage precludes the 1:2- $\text{H}_2$ -structure for the products. R. S. C.

**Quinoline derivatives.**—See B., 1943, III, 160.

$\alpha\beta$ -Unsaturated amino-ketones. VI. Mechanisms of the reactions of *sec*-amines with  $\alpha\beta$ -unsaturated  $\alpha$ -bromo-ketones. N. H. Cromwell and D. J. Cram. VII. Reaction of piperidine and benzylmethylamine with bromine derivatives of benzylideneacetone and -acetophenone. N. H. Cromwell and I. H. Witt. VIII. Reaction of primary amines with 1:3-diketones and bromine derivatives of benzylideneacetophenone. Ethyleneimines. N. H. Cromwell, R. D. Babson, and C. E. Harris (*J. Amer. Chem. Soc.*, 1943, 65, 301—308, 308—312, 312—315; cf. A., 1942, II, 149).—VI. Contrary to the literature (A., 1941, II, 271), *sec*-amines add to compounds,  $>\text{C}(\text{Br})\text{COR}$ , to give  $\alpha$ -bromo- $\beta$ -amino-ketones, which readily dissociate into their components and, under the influence of strong bases, rearrange to  $\alpha$ - $\text{NH}_2$ -ketones. The rearrangement probably proceeds by reversible formation (inhibited by presence of acid) of a salt,  $[\text{N}^+ \text{CH} \text{---} \text{CH} \text{---} \text{COR}] \text{Br}^-$ , which by interaction with other reagents leads to varied types of products. Tetrahydroisoquinoline (I) (prep. from isoquinoline by  $\text{H}_2$ -Cu chromite in  $\text{EtOH}$  at 180°/1800 lb.) and  $\text{CHPh} \cdot \text{CBr} \cdot \text{COMe}$  [prep. from  $\text{CHPhBr} \cdot \text{CHBr} \cdot \text{COMe}$  (II) by  $\text{NaOAc}$  in boiling 95%  $\text{EtOH}$ ], m.p. 30—31°, b.p. 114—117°/1 mm., in light petroleum- $\text{Et}_2\text{O}$  at -15° give  $\alpha$ -bromo- $\beta$ -tetrahydroisoquinolino- $\beta$ -phenylethyl Me ketone (III) (91%), m.p. 102—103°, which rapidly generates ionic  $\text{Br}$  in  $\text{EtOH}$  but only slowly in  $\text{HNO}_3 \cdot \text{EtOH}$ . With boiling  $\text{NaOEt} \cdot \text{EtOH}$ , (III) gives a tetrahydroisoquinolino- $\beta$ -phenylvinyl Me ketone (92%), m.p. 90—91°, unaffected by (I) in  $\text{EtOH}$ .  $\alpha\beta$ -Bistetrahydroisoquinolino- $\beta$ -phenylethyl Me ketone (IV), m.p. 169—170°, is obtained exothermally from (I) and (III) (75%) or (II) (63.4%) in  $\text{EtOH}$ . Tetrahydroquinoline (V) reacts with neither (II) nor (III). In  $\text{EtOH}$  at room temp. (III) and (V) give  $\beta$ -tetrahydroquinolino- $\alpha$ -tetrahydroisoquinolino- $\beta$ -phenylethyl Me ketone (43.7%; 30.5% formed in  $\text{Et}_2\text{O}$ ), m.p. 107—109°, which in boiling 15%  $\text{H}_2\text{SO}_4$  is hydrolysed to tetrahydroisoquinolinoacetone (VI) (hydrochloride, m.p. 213—215°), also obtained from (I) and  $\text{CH}_2\text{Cl} \cdot \text{COMe}$ . In  $\text{EtOH}$  at 0° morpholine and (III) give (IV) (27.9%) and an inseparable mixture of  $\alpha$ -tetrahydroisoquinolino- $\beta$ -morpholino- $\beta$ -phenylethyl Me ketone, (IV), and perhaps  $\alpha\beta$ -dimorpholino- $\beta$ -phenylethyl Me ketone; a mixture is also formed in  $\text{Et}_2\text{O}$ ; hydrolysis of the mixture gives (VI) as sole isolable product. Piperidine and (III) in  $\text{Et}_2\text{O}$  at 60° give only 5.3% of  $\beta$ -piperidino-tetrahydroisoquinolino- $\beta$ -phenylethyl Me ketone (VII), m.p. 150—51°; in  $\text{EtOH}$  only (IV) (19%) is isolated.  $\alpha$ -Bromo- $\beta$ -morpholino- $\beta$ -phenylethyl Me ketone (VIII) and (I) in  $\text{Et}_2\text{O}$  at 0° give (IV); in  $\text{EtOH}$  only 5.9% is obtained.  $\alpha$ -Bromo- $\beta$ -piperidino- $\beta$ -phenylethyl Me ketone (IX) and (I) in  $\text{Et}_2\text{O}$  or  $\text{EtOH}$  at 0° give (VII) (36.4 and

40.3%, respectively), which in 15%  $\text{H}_2\text{SO}_4$  at 100° gives  $\text{PhCHO}$ , piperidinoacetone [oxime, m.p. 122—123° (lit. 104°)], and a little  $\text{CH}_2\text{Ph} \cdot \text{CO} \cdot \text{COMe}$ . In  $\text{EtOH}$ , (V) and (IX) give exothermally 48.5% of (VII) (in  $\text{Et}_2\text{O}$ , 12.7%). In  $\text{EtOH}$  at room temp. (1 day), (III) gives (IV) (26%) and then, by treatment of the filtrate with morpholine at room temp.,  $\alpha\beta$ -dimorpholino- $\beta$ -phenylacetone (X) (5.5%), and 95% of the residual (III) is recovered. Similarly, (VIII) in  $\text{EtOH}$  with subsequent treatment with (I) gives (X) (15.3%) and then (IV) (31.4%). With  $\text{H}_2 \cdot \text{PtO}_2$  in  $\text{C}_6\text{H}_6$  at 28°/1.2 atm.,  $\alpha$ -bromo- $\beta$ -piperidino- $\beta$ -phenylpropionophenone gives piperidine (XI) and  $\text{Ph} \cdot [\text{CH}_2]_2 \cdot \text{COPh}$ ; with  $\text{I} \cdot \text{KI}$ -acid, complex condensation products containing no  $\text{Br}$  or  $\text{N}$  are formed.  $\alpha$ -Bromo- $\beta$ -piperidino- $\beta$ -phenylpropionophenone with  $\text{H}_2 \cdot \text{PtO}_2$  in  $\text{C}_6\text{H}_6$  at ~28°/1.2 atm. gives 82.7% of  $\text{CH}_2\text{Bz}_2$ .  $\alpha$ -Bromobenzylideneacetophenone and dry  $\text{HBr} \cdot \text{Et}_2\text{O}$  at -5° give  $\text{CHPhBr} \cdot \text{CHBr} \cdot \text{COPh}$ ;  $\alpha$ -piperidinobenzylideneacetophenone and dry  $\text{HBr} \cdot \text{C}_6\text{H}_6$  at 0° give piperidine hydrobromide.

VII.  $\text{COMe} \cdot \text{CH}_2\text{Bz}$  (1 mol.), (XI) (2 mols.), and conc.  $\text{HCl}$  (1 drop) at the b.p. give a small yield of  $\gamma$ -piperidino- $\alpha$ -phenyl- $\Delta\beta$ -buten- $\alpha$ -one, m.p. 97—98°, which in dil.  $\text{HCl}$  gradually gives  $\text{COMe} \cdot \text{CH}_2\text{Bz}$  (nearly 100%).  $\beta$ -Piperidinobenzylideneacetophenone does not condense with  $\text{CH}_2\text{Bz}_2$ .  $\text{CHPh} \cdot \text{CBr} \cdot \text{COMe}$  (XII) and (XI) in  $\text{Et}_2\text{O}$ -light petroleum at -30° give (IX), m.p. 80—82°, which gives ionic  $\text{Br}$  more rapidly in  $\text{EtOH}$  than in  $\text{HNO}_3 \cdot \text{EtOH}$  and with boiling  $\text{NaOEt} \cdot \text{EtOH}$  gives  $\alpha$ -piperidino- $\beta$ -phenylvinyl Me ketone, m.p. 56—58° (hydrolysed by acid to  $\text{CH}_2\text{Ph} \cdot \text{CO} \cdot \text{COMe}$ ). With (IV) in  $\text{EtOH}$ , (IX) gives  $\alpha$ -piperidino- $\beta$ -tetrahydroquinolino- $\beta$ -phenylethyl Me ketone, m.p. 126—127°.  $\text{CHPhBr} \cdot \text{CHBr} \cdot \text{COMe}$  (XIII) and (XI) in  $\text{EtOH}$  at room temp. give  $\alpha\beta$ -dipiperidino- $\beta$ -phenylethyl Me ketone, m.p. 121—122°.  $\alpha\beta$ -Di(benzylmethylamino)- $\beta$ -phenylethyl Me ketone, m.p. 106—108°, is obtained from  $\text{NHMe} \cdot \text{CH}_2\text{Ph}$  (XIV) by (XII) in  $\text{Et}_2\text{O}$ -light petroleum at -5° or (XIII) in  $\text{EtOH}$ .  $\text{CHPh} \cdot \text{CBr} \cdot \text{COPh}$  (XV) and (XIV) in  $\text{Et}_2\text{O}$ -light petroleum at 0° give  $\alpha$ -bromo- $\beta$ -benzylmethylamino- $\beta$ -phenylpropionophenone (XVI), m.p. 109—110° (slowly releases  $\text{I}$  from  $\text{HI}$ ; readily gives ionic  $\text{Br}$  in  $\text{EtOH}$ ), converted by  $\text{NaOEt} \cdot \text{EtOH}$  into  $\alpha$ -benzylmethylamino- $\beta$ -phenylacrylophenone, m.p. 73—75°, which in 5%  $\text{HCl}$  gives  $\text{CH}_2\text{Ph} \cdot \text{COBz}$ .  $\alpha\beta$ -Di(benzylmethylamino)- $\beta$ -phenylpropionophenone, m.p. 142—144°, is obtained (a) from (XIV) and (XV) in moist  $\text{Et}_2\text{O}$ , (b) with (?) an isomeride, m.p. 102—103°, from (XIV) and (XVI), or (c) in poor yield, with (?) 3-benzylmethylamino-2:4:5-triphenyl-1-methyl- $\Delta^3$ -pyrroline, m.p. 118—120°, from (XIV) and  $\text{CHPhBr} \cdot \text{CHBr} \cdot \text{COPh}$  in  $\text{EtOH}$ . In  $\text{EtOH}$ , (XVI) (1 mol.) and (V) (2 mols.) give  $\alpha$ -benzylmethylamino- $\beta$ -tetrahydroquinolino- $\beta$ -phenylpropionophenone, m.p. 150—153°, hydrolysed by acid to  $\omega$ -benzylmethylaminoacetophenone (oxime, m.p. 96—97°), which is also obtained from  $\text{COPh} \cdot \text{CH}_2\text{Br}$ . M.p. are corr. and determined in a preheated bath.

VIII. See A., 1943, II, 232.

R. S. C.

5:5-Disubstituted hydantoins. H. R. Henze, L. M. Long, R. J. Speer, and T. R. Thompson (*J. Amer. Chem. Soc.*, 1943, 65, 323—325).—Data of Marsh *et al.* (A., 1940, II, 289) are erroneous.  $\text{H}_2 \cdot \text{PtO}_2$  in  $\text{EtOH}$  reduces 5-phenyl- to 5-cyclohexyl-5-methylhydantoin, m.p. 214.6—215.8°.  $p\text{-NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COMe}$ ,  $\text{KCN}$ , and  $(\text{NH}_4)_2\text{CO}_3$  in 50%  $\text{EtOH}$  at 57—60° give 5-*p*-aminophenyl-5-methylhydantoin, m.p. 186—188°. Bucherer's method fails with  $p\text{-NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COPh}$ , but  $\text{KCN}$  and  $(\text{NH}_4)_2\text{CO}_3$  in fused  $\text{NH}_4\text{Ac}$  at 140° yield di-5-*p*-dimethylaminophenylhydantoin (38%) (colourless), m.p. 276—280°. Mesityl oxide gives a poor yield of 5-methyl-5- $\beta$ -methylpropenylhydantoin, having a low m.p. (identified by hydrogenation to the  $\text{Bu}^\beta$  compound), and 3-hydroxy-3:5:5-trimethylpyrrolidone, which is identified by conversion into 2-hydroxy- $\alpha\gamma$ -dimethyl- $\gamma$ -valerolactone (I) and is also obtained from diacetoneamine by aq.  $\text{KCN}$ .  $\text{COMe} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{OH}$  gives (I), 5:5-dimethyl- (probably formed by way of  $\text{COMe}_2$ ) and 5-methyl-5- $\beta$ -hydroxyisobutyl-hydantoin, m.p. 180—181°, and a substance, (?)  $\alpha$ -ureido- $\alpha\gamma$ -dimethyl- $\gamma$ -valerolactone, m.p. 209—210°. M.p. are corr.

R. S. C.

**Synthesis of pyrazolesulphanilamides. II.** G. Sanna [in part with (Signa.) V. Sollai] (*Gazzetta*, 1942, 72, 313—317; cf. Sanna, *Rend. Sem. Fac. Sci. Cagliari*, 1940, 10).—Antipyrine (I) with  $\text{ClSO}_3\text{H}$  gives the chloride (II), m.p. 191°, of 1-phenyl-2:3-dimethyl-5-pyrazolone-4-sulphonic acid, m.p. 277° [ $\text{NH}_4$  salt, m.p. 277°;  $\text{Cu}$  salt; amide, m.p. 229° [239°]]. With  $\text{CO}(\text{NH}_2)_2$ , (II) gives  $\text{NN}'$ -bis-(1-phenyl-2:3-dimethyl-5-pyrazolone-4-sulphon)carbamide, m.p. 165°. With 2-aminopyridine (III), (II) in  $\text{H}_2\text{O}$  at 100°, or at the m.p., gives 1-phenyl-2:3-dimethyl-5-pyrazolone-4-sulphon-2'-pyridylamide, m.p. 244°. (II) and (III) under other conditions [in  $\text{EtOH}$ ?] give a substance, m.p. 96°.  $p\text{-NH}_2\text{Ac} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Cl}$  and 4-aminoantipyrine give the  $\text{Ac}$  derivative, m.p. 267°, of 4-*p*-aminobenzenesulphonamidoantipyrine, m.p. 213°. (I) and  $\text{ClSO}_3\text{H}$  at 70°, followed by cooling, addition of  $\text{H}_2\text{O}$ , and reduction by  $\text{Zn}$ , give 4-thiolantipyrine, b.p. 135°/5 mm. E. W. W.

**Dinaphthylenedi-imine and dehydrodinaphthylenedi-imine.** A. Rieche, W. Rudolph, and R. Seifert (*Ber.*, 1940, 73, [B], 343—350).—1:1'-(8:8'-Diacetamido-2:2'-dinaphthone) and boiling aq.  $\text{H}_2\text{SO}_4$  (130°) give dehydrodinaphthylenedi-imine (dinylin) (I), m.p. 312°

(sulphate, m.p. 279—280°; ferrichloride;  $\text{CuCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{ZnCl}_2$ , and  $\text{SnCl}_2$  salts), also obtained from 2:2'-diamino-8:8-dimethoxy-1:1'-dinaphthyl and  $\text{FeCl}_3$  or  $\text{AlCl}_3$ . (I) with  $\text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  gel or  $\text{SiO}_2$  gel at  $\sim 300^\circ$  in  $\text{H}_2$  gives 1:1'-dinaphthylene 2:8'-2':8-dioxide, with  $\text{NaNO}_3\text{--H}_2\text{SO}_4$  at  $\geq 4^\circ$ , then at room temp., affords a  $\text{NO}_2$ -derivative, m.p. 344°, and with  $\text{Br--AcOH}$  gives a  $\text{Br}_2$ -compound, m.p.  $> 360^\circ$ . Aq.  $\text{NaOH--Na}_2\text{S}_2\text{O}_4$  at  $60^\circ$  converts (I) into (probably) a  $\text{H}_2$ -derivative, m.p.  $\sim 310^\circ$ , which forms salts with mineral acids. (I) and boiling  $\text{NH}_2\text{Ph}$  yield 3-anilinodinylin, m.p. 262°. 1:1'-(5:7:5':7'-Tetrachloro-8:8'-diacetamido-2:2'-dinaphthone) and boiling  $\text{H}_2\text{O--H}_2\text{SO}_4$  (1:2) give 5:7:5':7'-tetrachlorodinylin, m.p.  $> 360^\circ$ . A. T. P.

**Transformation of some oximinopyrroles into pyrimidine derivatives, Ciamician's reaction, and the constitution of nitrosopyrroles and pyrrole-aldehydes.** T. Ajello (*Gazzetta*, 1942, 72, 325—333).—The action of  $\text{PCl}_5$  on 4-oximino-2:3:5-triphenylpyrrole (I) to give  $\beta$ -benzamido- $\alpha\beta$ -diphenylacrylamide and thence 6-hydroxy-2:4:5-triphenylpyrimidine (cf. *ibid.*, 1940, 70, 460) proceeds by way of the hydrochloride of (I), which loses  $\text{H}_2\text{O}$  to give 4-chloroimino-2:3:5-triphenylpyrrole, as is shown by Zn reduction to the 4- $\text{NH}_2$ -compound. With  $\text{PCl}_5$ , 3-oximino-2:5-diphenylpyrrole gives  $\beta$ -benzamido- $\beta$ -phenylacrylamide, m.p.  $85^\circ$  (oxime, m.p.  $182^\circ$ , and hydrazone, m.p.  $196^\circ$ , both reduced to 6-amino-2:4-diphenylpyrimidine, m.p.  $120^\circ$ ), which when heated in  $\text{AcOH}$  or  $\text{EtOAc}$  slowly gives 6-hydroxy-2:4-diphenylpyrimidine. It is suggested that in the Ciamician reaction, a 2- $\text{CHCl}$  compound is intermediately formed. Nitrosopyrroles may have a  $\text{NN}'$ -oxide bridge, and an oxide bridge may explain the non-reactivity of pyrrole-aldehydes. E. W. W.

**Two heterovitamins- $B_1$ .** P. Baumgarten and A. Dornow (*Ber.*, 1940, 73, [B], 353—355).—Mainly a discussion of previous work (A., 1940, II, 291) and of structures. A. T. P.

**Triazines.**—See B., 1943, II, 213.

**Nucleic acids. XV. Synthesis of nucleotides (muscle-adenylic acid, cytidylic acid).** H. Brederick, E. Berger, and J. Ehrenberg (*Ber.*, 1940, 73, [B], 269—273).—Adenosine is converted by  $\text{CPh}_3\text{Cl}$  in dry  $\text{C}_5\text{H}_5\text{N}$  at  $100^\circ$  into triphenylmethylenadenosine,  $[\alpha]_D^{20} -17.6^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , transformed by  $\text{Ac}_2\text{O--C}_5\text{H}_5\text{N}$  at room temp. into the diacetate, which is hydrolysed by acid to adenosine diacetate, m.p.  $181\text{--}181^\circ$ . This is converted by  $\text{PPh}_2\text{OCl}$  in  $\text{C}_5\text{H}_5\text{N}$  followed by hydrolysis into muscle-adenylic acid in very small yield. Cytidine nitrate and  $\text{CPh}_3\text{Cl}$  in anhyd.  $\text{C}_5\text{H}_5\text{N}$  afford triphenylmethylenecytidine, similarly transformed into cytidylic acid, identified as the brucine salt,  $[\alpha]_D^{20} -15.3^\circ$  in 35%  $\text{EtOH}$ . H. W.

**Sedimentation and diffusion behaviour of nucleic acid preparations.** H. G. Tennent and C. F. Vilbrandt (*J. Amer. Chem. Soc.*, 1943, 65, 424—428).—The sedimentation velocity, diffusion consts., and apparent sp. vol. of eight nucleic acid preps. are determined and used to calculate mol. wts., frictional ratios, shape factors, and (for 5 preps. giving measurable sedimentation consts.) mol. dimensions. Three Na thymonucleates, prepared under very mild conditions, exist in solution as very long mols., having mol. wt.  $\sim 500,000$ . Thymonucleic and yeast nucleic acid, pancreas polynucleotide, and Ba thymate have mol. wt. 3000—7000. The cross-sectional diameter is  $\sim 15 \text{ \AA}$ , in agreement with X-ray dimensions ( $16 \times 7 \text{ \AA}$ ). R. S. C.

**Polymorphism of riboflavin.**—See A., 1943, I, 178.

**Aryldiazomorpholides.** R. A. Henry and W. M. Dehn (*J. Amer. Chem. Soc.*, 1943, 65, 479—480).—Benzene- (I), m.p.  $29\text{--}30^\circ$ , o-, m.p.  $32\text{--}33^\circ$ , and p-toluene-, m.p.  $49.5\text{--}50.5^\circ$ , naphthalene-a-, m.p.  $82\text{--}83^\circ$ , and - $\beta$ - (II), m.p.  $99.5\text{--}100.5^\circ$ , m-xylene-2-, an oil, diphenyl-4-, m.p.  $110.5\text{--}111^\circ$ , m-, m.p.  $83\text{--}84^\circ$ , and p-nitrobenzene-, m.p.  $137.5\text{--}138.5^\circ$ , o-, m.p.  $20\text{--}22^\circ$ , m-, an oil, and p-chlorobenzene-, m.p.  $54\text{--}55^\circ$ , 2:5-dichlorobenzene-, m.p.  $76\text{--}77^\circ$ , m-, m.p.  $33\text{--}34^\circ$ , and p-bromobenzene- (III), m.p.  $89.5\text{--}90^\circ$ , p-iodobenzene-, m.p.  $140.5\text{--}141.5^\circ$ , m-chlorotoluene-6-, m.p.  $59\text{--}60^\circ$ , m-bromotoluene-4-, m.p.  $48.5\text{--}49.5^\circ$ , 2:6-dibromotoluene-4-, m.p.  $87\text{--}88^\circ$ , p-anisole- (IV), m.p.  $69\text{--}70^\circ$ , and p-morpholinobenzene- (V), m.p.  $209\text{--}211^\circ$ , diazomorpholide and diphenyl-pp-, m.p.  $253\text{--}255^\circ$ , and 3:3'-dimethyldiphenyl-4:4'-bisdiazomorpholide, m.p.  $140.5\text{--}141.5^\circ$ , are prepared. Excepting (IV), they are stable when solid. In conc.  $\text{HBr}$  or  $\text{HCl}$ , (V) gives 4-p-bromophenylmorpholine hydrobromide, m.p.  $114.5\text{--}115.5^\circ$ , or hydrochloride, decomp.  $192\text{--}194^\circ$ , respectively. With  $\text{C}_6\text{H}_6$  and  $\text{AcOH}$  (1 mol.) or, better,  $\text{C}_6\text{H}_6\text{--AlCl}_3$ , they give  $\text{Ph}_2$  derivatives. They are unaffected by  $\text{Ac}_2\text{O}$ . With aq.  $\text{HIO}_4$ , (III) gives I, p- $\text{C}_6\text{H}_4\text{BrI}$  (7%), p- $\text{C}_6\text{H}_4\text{I--NO}_2$ , and tar. With  $\text{SO}_2$ , (I), (II), and (III) give products, m.p.  $142\text{--}143.5^\circ$ ,  $181\text{--}182.5^\circ$ , and  $155\text{--}156^\circ$ , respectively, insol. in but decomposed by hot conc.  $\text{HCl}$ , sol. and slowly decomp. in cold aq. alkali. In boiling aq.  $\text{NaOH}$ , the product from (III) gives p- $\text{C}_6\text{H}_4\text{Br--SO}_2\text{H}$ . M.p. are corr. R. S. C.

**High mol. wt. aliphatic compounds of nitrogen and sulphur.**—See A., 1943, II, 218.

I (A., II.)

**Thiazans.**—See B., 1943, II, 212.

**Transformation of pyrrole- into isooxazole-derivatives.** T. Ajello and (Signa.) C. Petronici (*Gazzetta*, 1942, 72, 333—342).—2:3:5-Trimethylpyrrole with Na and  $\text{C}_8\text{H}_{11}\text{O--NO}$  gives the Na salt (I) of 4-oximino-2:3:5-trimethylpyrrole, amorphous, which is isolated by action of aq.  $\text{CO}_2$ . With boiling 0.5N- $\text{HCl}$ , (I) gives 3-acetyl-4:5-dimethylisooxazole (II), b.p.  $190\text{--}195^\circ/759 \text{ mm}$ . [oxime (III), m.p.  $180^\circ$  ( $168^\circ$ ?) (Bz derivative, m.p.  $123^\circ$ ); semicarbazone (IV), m.p.  $249^\circ$ ; phenylhydrazone, m.p.  $156^\circ$ ; azine, m.p.  $124^\circ$ ], which with boiling aq.  $\text{HNO}_3$  gives 4:5-dimethylisooxazole-3-carboxylic acid, m.p.  $154^\circ$ . With  $\text{NH}_2\text{OH.HCl}$  in  $\text{H}_2\text{O--EtOH}$  at  $100^\circ$ , (I) gives  $\gamma$ -methylhexane- $\beta\delta\epsilon$ -trione trioxime (V), m.p.  $168^\circ$  (Bz derivative, m.p.  $138^\circ$ ). With boiling  $\text{KOH--EtOH--H}_2\text{O}$ , (V) gives the oxime, m.p.  $73^\circ$ , of 3-methyl-4- $\beta$ -keto-sec-butyl-1:2:5-oxadiazole, an oil (semicarbazone, m.p.  $165^\circ$ ), which is hydrolysed by boiling 50%  $\text{KOH--EtOH}$  to  $\text{AcOH}$  and 3-methyl-4-ethyl-1:2:5-oxadiazole, an oil (oxidised to 3-methyl-1:2:5-oxadiazole-4-carboxylic acid). With  $\text{EtOH--HCl}$ , (V) gives, after brief heating, (III), and, after longer heating, (II). With aq.  $\text{NH}_2\text{CO--NH--NH}_2\text{HCl}$  at  $100^\circ$ , (I) gives  $\gamma$ -methylhexane- $\beta\delta\epsilon$ -trione  $\beta\epsilon$ -disemicarbazone  $\delta$ -oxime, m.p.  $234^\circ$ , hydrolysed by boiling conc.  $\text{HCl}$  to (IV). E. W. W.

**Absorption and resonance in dyes.**—See A., 1943, I, 192.

**Effects of environment and aggregation on absorption spectra of dyes.**—See A., 1943, I, 192.

**Colour and constitution of polymethine dyes.**—See A., 1943, I, 192.

## VII.—ALKALOIDS.

**Veratrine alkaloids. XV. Rubijervine and isorubijervine.** W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1943, 148, 41—50).—Accumulated analytical data indicate that jervine, rubijervine (I), and probably germine are  $\text{C}_{27}$  alkaloids built up on the same general hydrocarbon ring which is probably identical with or closely related to that of the sterols. The isolation of (I), m.p.  $240\text{--}242^\circ$ ,  $[\alpha]_D^{25} +19.0^\circ$  in  $\text{EtOH}$ , from the final viscous mother-liquors from the hellebore roots by hydrolysis followed by treatment with  $\text{CHCl}_3$  is described. (I) is accompanied by isorubijervine,  $\text{C}_{27}\text{H}_{43}\text{O}_2\text{N}$ , m.p.  $235\text{--}237^\circ$ ,  $[\alpha]_D^{25} +6.5^\circ$  in  $\text{EtOH}$ , or (+ $\text{EtOH}$ ), m.p.  $215\text{--}217^\circ$  (hydrobromide, sinters  $> 275^\circ$ , softens to a resin at  $290\text{--}295^\circ$ ). (I) gives a hydrobromide, m.p. (indef.)  $265\text{--}270^\circ$ , a hydriodide, m.p.  $293\text{--}296^\circ$  after softening, and an  $\text{Ac}_2$  derivative, m.p.  $160\text{--}163^\circ$ . The basic fraction obtained by dehydrogenation (Se) of (I) is essentially 5-methyl-2-ethylpyridine; there is no evidence of cevantharidine. The neutral fraction contains a relatively large hydrocarbon fraction  $\text{C}_{18}\text{H}_{18}$ , m.p.  $74\text{--}77^\circ$  [picrate, m.p.  $131\text{--}132^\circ$ ; additive compound, m.p.  $144\text{--}145^\circ$ , with  $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ ], probably a methylcyclopentenophenanthrene (suggested also by absorption spectrum), and a phenol,  $\text{C}_{18}\text{H}_{18}\text{O}$ , m.p.  $136\text{--}138^\circ$ . H. W.

**Veratrine alkaloids. XVI. Formulation of jervine.** W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1943, 148, 51—55).—Analyses of jervine (I), m.p.  $237\text{--}238^\circ$  after softening,  $[\alpha]_D^{25} -147^\circ$  in  $\text{EtOH}$ , its hydrochloride, parallelograms, m.p.  $330\text{--}334^\circ$  (decomp.) after changing to needles at  $280^\circ$ , hydriodide, m.p.  $302\text{--}305^\circ$ , nitroso-, m.p.  $250\text{--}253^\circ$ , N-acetyl-, m.p.  $224\text{--}225^\circ$ , softens at  $210^\circ$ , and diacetyl-jervine, m.p.  $147\text{--}153^\circ$  from dil.  $\text{COMe}_2$  or  $154\text{--}163^\circ$  from  $\text{MeOH}$ , support the formula  $\text{C}_{27}\text{H}_{39}\text{O}_3\text{N}$  for the base. (I) liberates 4 mols. of  $\text{CH}_4$  at  $95^\circ$  (Zerevitinov) and hence probably contains 1 reactive and 2 sluggish OH. (I) is reduced by Na in  $\text{BuOH}$  to tetrahydrojervine, m.p.  $227\text{--}229^\circ$ , which does not yield a sparingly sol. sulphate, but by  $\text{H}_2\text{--PtO}_2$  in  $\text{AcOH}$  to a mixture of isomerides from which tetrahydrojervines, m.p.  $228\text{--}232^\circ$  (sparingly sol. sulphate) and m.p.  $210\text{--}212^\circ$ , are isolated. H. W.

**Veratrine alkaloids. XVII. Germine; its formulation and degradation.** L. C. Craig and W. A. Jacobs (*J. Biol. Chem.*, 1943, 148, 57—66; cf. Poethke, A., 1938, II, 35).—It is shown that germine (I) is  $\text{C}_{27}\text{H}_{43}\text{O}_8\text{N}$  and is therefore isomeric with cevine (II). The mother-liquor from the directly crystallising alkaloids of *Veratrum album* is hydrolysed and treated with  $\text{CHCl}_3$ , giving a cryst. compound of  $\text{CHCl}_3$  and (I) contaminated with rubijervine, which is removed by crystallisation from  $\text{MeOH}$ . (I) (+2 $\text{MeOH}$ ), m.p.  $\sim 220^\circ$  after softening (decomp.) at  $\sim 163\text{--}173^\circ$ ,  $[\alpha]_D^{25} +5.0^\circ$  in 95%  $\text{EtOH}$ , contains 8 active H (Tschugaev-Zerevitinov) as does (II). (I) and  $\text{COMe}_2$  in  $\text{EtOH}$  containing  $\text{HCl}$  afford acetonyl-[isopropylidene]-germine, m.p.  $235\text{--}239^\circ$  (decomp.) after softening and becoming discoloured [hydrochloride, m.p.  $275^\circ$  (decomp.), shrinks at  $255^\circ$ ]. The mother-liquors from (I) contain isogermine, m.p.  $260^\circ$ , darkens  $> 245^\circ$ , sinters  $> 250^\circ$ ,  $[\alpha]_D^{25} +46.5^\circ$  in  $\text{EtOH}$ . (I) is oxidised by  $\text{CrO}_3\text{--H}_2\text{SO}_4$  at room temp. and subsequently at  $95^\circ$  to  $\text{Me}_4$  hexanetetracarboxylate, m.p.  $63\text{--}64^\circ$ ,  $[\alpha]_D^{25} +21^\circ$  in  $\text{MeOH}$ , obtained previously from (II); no indication of the production of the precursor of decevinic acid was obtained. The main, volatile basic product of the dehydrogenation (Se) of (I) is 5-methyl-2-ethylpyridine. The volatile hydrocarbon fraction prob-

ably contains  $C_{18}H_{18}$ . The undistilled dehydrogenation mixture affords cevanthridine and cevanthrol.

Protoveratrine is hydrolysed to a cryst. *alkamine*,  $C_{27}H_{43}O_9N$ , which is shown to contain a double linking by reduction to *dihydroprotoverine*,  $C_{27}H_{45}O_9N$ . Similarly (I) affords *dihydrogermine*. These *tert.* bases, like (II) and solanidine, must be hexacyclic compounds. H. W.

**Adsorption in relation to constitution.** Adsorption of alkaloids by silica gel.—See A., 1943, I, 199.

## VIII.—ORGANO-METALLIC COMPOUNDS.

**Mercuri-compounds.**—See B., 1943, III, 161.

**Modern methods of preparative organic chemistry. I. Syntheses with organic lithium compounds.** G. Wittig (*Angew. Chem.*, 1940, 53, 241—247).—A review.

## IX.—PROTEINS.

**Structure of the protein molecule.**—See A., 1943, I, 194.

**Periodic structure of proteins.** A. G. Ogston (*Trans. Faraday Soc.*, 1943, 39, 151—158).—The theory of Bergmann and Niemann (A., 1937, III, 168; 1938, III, 210) is examined mathematically, and the numerical conditions that must be fulfilled by a regular periodic structure are established. A simple diagrammatic test, requiring full analytical data and applicable to complex structures, is described. F. L. U.

**Absence of  $\beta$ -alanine from proteins.** M. A. Pollack (*J. Amer. Chem. Soc.*, 1943, 65, 484—485).—Since the hydrolysates from silk fibroin, horse haemoglobin, ovalbumin, gelatin, casein, and lactoglobulin possess no growth-promoting properties for yeast, the proteins do not contain  $\beta$ -alanine. R. S. C.

**Simple method for the approximate estimation of the isoelectric point of soluble proteins.**—See A., 1943, III, 517.

**Denaturation of fibrinogen by anticoagulants.**—See A., 1943, III, 372.

## X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

**Oxidative degradation of halogen-substituted spruce-lignins.** W. Lautsch and G. Piazzolo (*Ber.*, 1940, 73, [B], 317—320).—Bromolignin and boiling  $Co(OH)_3$  (from  $CoSO_4 \cdot 7H_2O$ -aq.  $NaOH-H_2O_2$ ) + 10% aq.  $KOH$  (in  $O_2$ ) afford 6-bromovanillin (8% yield), m.p. 176°, and a little vanillin. Iodolignin, obtained by the action of  $KI-I$  on the  $OAc-Hg$ -compound, similarly yields 10% of 5-iodovanillin (cf. Freudenberg *et al.*, A., 1940, II, 352). Structural aspects are discussed. A. T. P.

**Fine structure of lignins.**—See A., 1943, I, 195.

## XI.—ANALYSIS.

**Micro-analytical determination of oxygen.** J. Unterzaucher (*Ber.*, 1940, 73, [B], 391—404).—Schütze's method (A., 1940, II, 199) is improved. A. T. P.

**Determination of sulphur in organic compounds by hydrogenation.** W. Theilacker and W. Schmid (*Angew. Chem.*, 1940, 53, 255—256).—The ter Meulen method is improved by using platinised  $SiO_2$  wool with a modified absorption train. A  $SiO_2$  reaction tube is necessary only for cyclic S compounds (e.g., thianthren), where bright red heat is needed. M. H. M. A.

**Micro-extraction and micro-titration of fatty acids.** D. Stretten and G. F. Grail (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 300).—8—20-mg. samples of fatty acids are titrated using 0.16N- $NaOH$  delivered from a micrometer-driven micro-burette, *a*-naphtholphthalein indicator, and 90%  $MeOH$  as solvent for acid and alkali. A micro-extraction apparatus for extraction of fatty acids is described. J. D. R.

**Separation of acetic, butyric, lactic, and *d*-gluconic acid.** S. Preiss (*Biochem. Z.*, 1940, 306, 130—136).—In a modification of the procedure of Wiegner and Magasanik (A., 1922, ii, 532),  $PrCO_2H$  and most of the  $AcOH$  are separated from the other acids by repeated distillation. When the residue is continuously extracted with  $Et_2O$  for 24 hr., lactic acid and the remainder of the  $AcOH$  are removed and determined after evaporation of the  $Et_2O$ , by addition of excess of alkali and titration with acid. *d*-Gluconic acid (insol. in  $Et_2O$ ) is determined in the same way in the residue from the  $Et_2O$  extraction. W. McC.

**Ascorbic acid. I. Detection and estimation.** W. R. Fearon and E. Kawerau (*Sci. Proc. Roy. Dublin Soc.*, 1943, 23, 103—110).—Available methods for the detection and determination of ascorbic acid (I), dehydroascorbic acid (II), and "bound" ascorbic acid are classified and discussed. (I) is detected by the development of a violet colour with  $o-C_6H_4(NO_2)_2$  and 20%  $NaOH$ ; the test is not given under defined conditions by (II), glutathione, cysteine, creatinine, or uric acid and only more slowly by reducing sugars. (II) in solution buffered to pH 4 gives a stable, grass-green colour when gently boiled; the test is not given by (I) or by any of the familiar biological acids, sugars, proteins, and related substances. (I) is determined by titration with standard  $Fe^{+++}$  solution in presence of  $AcOH$ ; 1%  $KCNS$  is used as indicator. (I) can also be determined by titration with I using xylene as a partition indicator. H. W.

**N-Benzylamides as derivatives for identifying the acyl group in esters.** O. C. Dermer and J. King (*J. Org. Chem.*, 1943, 8, 168—173).—Many esters and free acids can be converted into cryst. N-benzylamides by boiling  $CH_2Ph-NH_2$  in presence of salt catalysts (e.g.,  $NH_4Cl$ ). The method fails for esters of inorg. acids, sulphonic acids,  $CO$ -acids, polynitro-aromatic acids, and some halogenated fatty acids. Esters of alcohols of high mol. wt. may require preliminary methanolysis. The amides formed by  $OH$ -acids,  $OAlk$ -acids, and polybasic acids, or by their respective esters, constitute excellent identifying derivatives whereas those from fatty acids melt too low and too close together to be useful. The following *-benzylamides* are new: *a*-methyl-*n*-butyr-, m.p. 47.5—48.5°; *isovaler*-, m.p. 53—54°; *m*-tolu-, m.p. 74.5—75.5°; *a*-ethyl-*n*-butyr-, m.p. 76—77°; *phenoxyacet*-, m.p. 84.5—86.0°; *myrist*-, m.p. 89—90°; *p*-aminobenz-, m.p. 89—90°; *glycoll*-, m.p. 103—104°; *o*-iodobenz-, m.p. 109—110°; *anilinoacet*-, m.p. 113—114°; *diglycoll*-, m.p. 124.0—124.5°; *anthranil*-, m.p. 124—125°; *ethylmalon*-, m.p. 137—138°; *diethylmalon*-, m.p. 137.5—138.5°; *m*-hydroxybenz-, m.p. 141—142.5°; *2-furylacryl*-, m.p. 145—146°; *n*-butylmalon-, m.p. 148—149°; *male*-, m.p. 149—150°; *pinel*-, m.p. 153—154°; *sebac*-, m.p. 166.0—167.5°; *phenylethylmalon*-, m.p. 167—168°; *citr*-, m.p. 169—170°; *glutar*-, m.p. 169.5—170°; *p*-nitrophenylacet-, m.p. 185—186°; *adip*-, m.p. 188—189°; *phenylsuccin*-, m.p. 189—190°; *naphthal*-, m.p. 196.5—197.5°; *fumar*-, m.p. 203.5—205°; *cinnam*-, m.p. 225—226°; *terephthal*-, m.p. 264—266°.  $\beta$ -Benzylaminopropionbenzylamide hydrochloride (from  $CH_2CH_2CO_2Me$ ) has m.p. 236—237°. M.p. are corr. H. W.

**Chromatography as a means of separating amino-acids.** J. L. Wachtel and H. G. Cassidy (*J. Amer. Chem. Soc.*, 1943, 65, 665—668; cf. A., 1942, II, 249).—Details are given for separating glycine, leucine, phenylalanine, and tyrosine by chromatography on C from  $H_2O$ . The mixture is separated on one column into (a) the first two and (b) the second two acids named and these pairs are then separated on further columns. Some of the tyrosine is lost by decomp. R. S. C.

**Sugar analysis by alkaline ferricyanide method. Determination of ferrocyanide by iodometric and other procedures.** D. T. Englis and H. C. Becker (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 262—264).— $K_4Fe(CN)_6$  is oxidised with I in acid solution in presence of  $PO_4^{+++}$  or  $F^-$  to remove Fe and prevent the reverse reaction. Room temp. with 60—75% excess of I for 15 min. is used, and the vol. is adjusted to give  $[K_3Fe(CN)_6] < 0.01M$ . The excess of I is titrated with  $Na_2S_2O_3$ . A comparison of the results obtained on the reduction of alkaline  $K_3Fe(CN)_6$  by glucose and fructose, by direct oxidation of  $K_4Fe(CN)_6$  by I, by indirect determination of  $K_3Fe(CN)_6$  iodometrically, and by direct oxidation of  $K_4Fe(CN)_6$  with  $Ce(SO_4)_2$  shows good agreement and indicates that the by-products of the primary oxidation of sugars have a negligible effect on any of the methods used to determine  $K_3Fe(CN)_6$  consumed. J. D. R.

**Micro-colorimetric determination of tryptophan.** H. W. Eckert (*J. Biol. Chem.*, 1943, 148, 205—212).—The sample is dissolved in 1.2N- $HCl$  and treated with 1%  $NaNO_2$ ; after 30 min. 4%  $NH_2 \cdot SO_3NH_4$  is added followed after 10 min. with 10 c.c. of  $H_2O$  and finally 0.1%  $NH_2 \cdot [CH_2]_2 \cdot NH \cdot C_{10}H_7 \cdot a, 2HCl$  (I). The red colour attains max. intensity in 30—60 min. If the material is colourless, the blank consists of 1.2N- $HCl$  treated in the same way. If the sample gives a colour other than red, a close approximation may be secured by adding a small amount of  $Na_2SO_3$  to the coloured solution after the reading on the colorimeter is taken. After the red colour has disappeared the blank reading is made. Similarly the addition of  $KH_2PO_4$  and  $NaNO_2$  will discharge the red colour, or the sample may be treated exactly and described except that in the last step 5 c.c. of  $H_2O$  are added in place of (I). If these methods are inadequate, the mixtures are extracted with  $Bu^aOH$  and the filtered extracts are examined colorimetrically. H. W.

**Spectrophotometric analysis of tissue staining.**—See A., 1943, III, 554.

## A., II.—Organic Chemistry

SEPTEMBER, 1943.

## I.—ALIPHATIC.

Manufacture of hydrocarbons by alkylation.—See B., 1943, II, 237.

Polymerisation of olefines with a phosphoric acid catalyst.—See B., 1943, II, 238.

Substituted acetylenes and their derivatives. XLV. Addition of hydrogen to multiple carbon-carbon linkings. IV. Electrolytic reduction of alkyl- and aryl-acetylenes. K. N. Campbell and E. E. Young (*J. Amer. Chem. Soc.*, 1943, 65, 965—967; cf. A., 1941, II, 71).—Electrolytic reduction of  $n\text{-C}_5\text{H}_{11}\cdot\text{C}\equiv\text{CH}$ ,  $(\text{CPr}^a)_2$ ,  $(\text{CBu}^a)_2$ , or  $(\text{CPh})_2$  at a spongy Ni cathode (100% current efficiency at  $>$  a small, limiting c.d.) gives  $\text{cis-}(\text{CHR})_2$ , but  $\text{CPh}\cdot\text{CH}$  gives  $\text{CHPh}\cdot\text{CH}_2 + \text{PhEt}$ . At a Cu cathode  $(\text{CPr}^a)_2$  is reduced only slowly and in poor yield. Alkylacetylenes are not reduced at Cd, Pb, or Pb-Hg cathodes. R. S. C.

Mechanism of reaction between  $n$ -butyl bromide and hydroxylic solvents.—See A., 1943, I, 231.

Preparation of acetylenic alcohols.—See B., 1943, II, 239.

Polyene series. VIII. New anionotropic rearrangement. Isomerisation of acetylenylcarbinols from  $\alpha\beta$ -unsaturated aldehydes. E. R. H. Jones and J. T. McCombie. IX. Condensation product of  $\Delta^a$ -hexinene with crotonaldehyde and its anionotropic rearrangement. I. M. Heilbron, E. R. H. Jones, and R. A. Raphael. X. Condensation of  $\gamma$ -methyl- $\Delta^{\beta\delta}$ -pentenine ( $\alpha\beta$ -dimethylvinylacetylene) with butaldehyde, crotonaldehyde, and citral. Anionotropic rearrangements with vinylacetylenecarbinols derived from  $\alpha\beta$ -unsaturated aldehydes. I. M. Heilbron, A. W. Johnson, E. R. H. Jones, and R. A. Raphael. XI. Anionotropic rearrangements of the acetylenic glycol from crotonaldehyde. I. M. Heilbron, E. R. H. Jones, and R. A. Raphael (*J.C.S.*, 1943, 261—264, 264—265, 265—268, 268—270).—VIII. With 5%  $\text{H}_2\text{SO}_4$  at  $20^\circ$  in  $\text{N}_2$ ,  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{C}\equiv\text{CH}$  (I) yields  $\Delta^{\gamma\epsilon}$ -hexeninen- $\beta$ -ol (II), b.p.  $69\text{--}70^\circ/18$  mm. [2 active H per mol. (Zerevitinov); phenylurethane, m.p.  $83\text{--}84^\circ$ ;  $\beta$ -naphthylurethane, m.p.  $77\text{--}78^\circ$ ; acetate, b.p.  $101\text{--}103^\circ/70$  mm.], reduced ( $\text{H}_2$ , Pd-norite in MeOH) to  $\text{CHMeBu}^a\cdot\text{OH}$ , oxidised ( $\text{CrO}_3$  in  $\text{H}_2\text{O}$ - $\text{AcOH}$ - $\text{H}_2\text{SO}_4$ ) to  $\text{COMeBu}^a$ .  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{C}\equiv\text{CH}$  yields  $\beta$ -methyl- $\Delta^{\gamma\epsilon}$ -hexeninen- $\beta$ -ol (III), b.p.  $91\text{--}93^\circ/50$  mm. (phenylurethane, m.p.  $95\text{--}95.5^\circ$ ), reduced to  $\text{CMe}_2\text{Bu}^a\cdot\text{OH}$  (phenylurethane, m.p.  $44\text{--}45^\circ$ ).  $\text{CHMe}\cdot\text{CMe}\cdot\text{CH}(\text{OH})\cdot\text{C}\equiv\text{CH}$  yields  $\gamma$ -methyl- $\Delta^{\gamma\epsilon}$ -hexeninen- $\beta$ -ol (IV), b.p.  $78\text{--}81^\circ/20$  mm. ( $\alpha$ -naphthylurethane, m.p.  $93\text{--}94^\circ$ ), reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ ) to  $\text{CHMePr}^a\cdot\text{CHMe}\cdot\text{OH}$ , oxidised ( $\text{CrO}_3$ -dil.  $\text{H}_2\text{SO}_4$ ) to  $\text{COMe}\cdot\text{CHMePr}^a$ , and  $\text{CHPr}^a\cdot\text{CET}\cdot\text{CH}(\text{OH})\cdot\text{C}\equiv\text{CH}$  yields  $\epsilon$ -ethyl- $\Delta^{\epsilon\eta}$ -octeninen- $\delta$ -ol (V), b.p.  $100\text{--}101.5^\circ/14$  mm. ( $\alpha$ -naphthylurethane, m.p.  $75\text{--}76^\circ$ ). (II), (III), (IV), and (V) show characteristic absorption max. at  $2230\text{--}2270$   $\mu$ . The rate of isomerisation of (I) in the presence of various concns. of  $\text{H}_2\text{SO}_4$  and of other acids has been studied by means of absorption measurements.

IX.  $\Delta^{\beta\epsilon}$ -Deceninen- $\delta$ -ol, b.p.  $90^\circ/1$  mm. (VI) [from  $\Delta^a$ -hexinene, with Na in liquid  $\text{NH}_3$  followed by  $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$  (30%), or with  $\text{MgEtBr}$  in boiling  $\text{Et}_2\text{O}$ , followed by  $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$  (80% yield)] (1 active H per mol.;  $\alpha$ -naphthylurethane, m.p.  $69^\circ$ ), is reduced ( $\text{H}_2$ , Pd-norite in MeOH) to  $\text{C}_6\text{H}_{13}\cdot\text{CHPr}\cdot\text{OH}$  (3 : 4-dinitrobenzoate, m.p.  $24^\circ$ ), oxidised to  $\text{COPr}\cdot\text{C}_6\text{H}_{13}$  [semicarbazone, m.p.  $56^\circ$  (or  $51^\circ$ , depending on rate of heating) (lit.  $51\text{--}52^\circ$ )]. (VI) with 25%  $\text{H}_2\text{SO}_4$  at  $20^\circ$  in  $\text{N}_2$  yields  $\Delta^{\gamma\epsilon}$ -deceninen- $\beta$ -ol, b.p.  $113\text{--}114^\circ/3$  mm., absorption max. at  $2260$   $\mu$ . (1 active H per mol.;  $\alpha$ -naphthylurethane, m.p.  $65^\circ$ ), reduced to  $\text{C}_8\text{H}_{17}\cdot\text{CHMe}\cdot\text{OH}$  (3 : 5-dinitrobenzoate, m.p.  $44^\circ$ ), oxidised to  $\text{COMe}\cdot\text{C}_8\text{H}_{17}$ .

X.  $\text{CHMe}\cdot\text{CMe}\cdot\text{C}\equiv\text{CH}$  condenses with  $\text{Pr}^a\text{CHO}$ ,  $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ , and citral by the Grignard method (or, in the second case, the Na method) yielding respectively  $\eta$ -methyl- $\Delta^{\gamma\epsilon}$ -noneninen- $\delta$ -ol, b.p.  $106^\circ/15$  mm. (1 active H per mol.; 3 : 5-dinitrobenzoate, m.p.  $53^\circ$ ;  $\beta$ -naphthylurethane, m.p.  $46^\circ$ ), reduced ( $\text{H}_2$ ,  $\text{PtO}_2$  in MeOH) to  $\eta$ -methyl-nonan- $\delta$ -ol (VII), b.p.  $94^\circ/12$  mm. (3 : 5-dinitrobenzoate, m.p.  $60^\circ$ ), oxidised to  $\eta$ -methylnonan- $\delta$ -one, b.p.  $86^\circ/11$  mm. (phenylsemicarbazone, m.p.  $65^\circ$ ),  $\eta$ -methyl- $\Delta^{\beta\gamma\epsilon}$ -nonadieninen- $\delta$ -ol (VIII), b.p.  $127^\circ/16$  mm. (1 active H per mol.;  $\alpha$ -phenylurethane, m.p.  $98^\circ$ ), reduced to (VII), and a slightly impure carbinol (IX) (0.9 active H per mol.), reduced ( $\text{PtO}_2$ ) to  $\beta$ , $\gamma$ , $\lambda$ -trimethyl- $n$ -tridecane, b.p.  $152^\circ/16$  mm. (VIII) with 5%  $\text{H}_2\text{SO}_4$  at  $20^\circ$  in  $\text{N}_2$  yields  $\eta$ -methyl- $\Delta^{\gamma\epsilon}$ -nonadieninen- $\beta$ -ol, b.p.  $122^\circ/16$  mm. (0.95 active H per mol.;  $\alpha$ -naphthylurethane, m.p.  $82^\circ$ ), reduced ( $\text{PtO}_2$ ) to  $\eta$ -methylnonan- $\beta$ -ol, b.p.  $93^\circ/4$  mm.

(3 : 5-dinitrobenzoate, m.p.  $65^\circ$ ), oxidised to the ketone, b.p.  $116^\circ/6$  mm. (semicarbazone, m.p.  $124^\circ$ ; phenylsemicarbazone, m.p.  $95.5^\circ$ ). (IX) on distillation undergoes rearrangement and dehydration, giving  $\text{C}_{14}\text{H}_{22}$ . Absorption details are given.

XI.  $\text{MgEtBr}$  in  $\text{Et}_2\text{O}$  with  $\text{C}_2\text{H}_2$ , followed by  $\text{CMe}\cdot\text{CH}\cdot\text{CHO}$ , yields  $\Delta^{\beta\theta\epsilon}$ -decadieninen- $\delta$ -diol, converted by 10%  $\text{H}_2\text{SO}_4$  at  $20^\circ$  in  $\text{N}_2$  into  $\Delta^{\gamma\eta\epsilon}$ -decadieninen- $\beta$ -diol, b.p.  $65\text{--}70^\circ$  (bath temp.)/ $10^{-4}$  mm. (from which a pure isomeride, m.p.  $56.5\text{--}57^\circ$ , was isolated) (1.9 active H per mol.; diacetate, b.p.  $131\text{--}132^\circ/10^{-3}$  mm.; bisphenylurethane, m.p.  $181^\circ$ ), reduced ( $\text{PtO}_2$ ) to decane- $\beta$ -diol, b.p.  $114^\circ/5$  mm. (2.1 active H per mol.; bisphenylurethane, m.p.  $134^\circ$ ), oxidised to decane- $\beta$ -dione, m.p.  $62^\circ$  (dioxime, m.p.  $132^\circ$ ), further oxidised ( $\text{NaOBr}$ ) to suberic or ( $\text{HNO}_3$ ) to adipic acid. Absorption details are given. A. Li.

By-product  $\alpha\gamma$ -butylene glycol. J. B. Cloke and R. M. Wolff (*J. Amer. Chem. Soc.*, 1943, 65, 986—987).—An acetate of  $\text{OH}\cdot\text{CHMe}\cdot[\text{CH}_2]_2\cdot\text{OH}$  (I), obtained as a by-product (4—6%) in the prep. of  $\text{EtOAc}$  from  $\text{MeCHO}$  and  $\text{Al}(\text{OEt})_3$ , is converted into (I) by slow fractional distillation with a little conc.  $\text{HCl}$  in  $\text{MeOH}$  or  $\text{EtOH}$ . R. S. C.

Esterification of allyl-type alcohols and products resulting therefrom.—See B., 1943, II, 240.

Concrete oil of jasmine flowers.—See A., 1943, III, 540.

Carbohydrates. VI. Constitution of styracitol. Transformation of aldoses into ketoses. L. Zervas and I. Papadimitriou (*Ber.*, 1940, 73, [B], 174—176).—Styracitol (I) is shown to be  $\alpha$ -anhydromannitol (A). A new transition from the aldose to the ketose series is described. (I) is transformed by successive treatments with  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  and  $\text{BzCl}$  in anhyd.  $\text{C}_5\text{H}_5\text{N}$  into styracitol  $\beta\gamma\delta$ -tribenzoate  $\zeta$ -p-toluenesulphonate (II), m.p.  $162^\circ$ ,  $[\alpha]_D^{20} -166.5^\circ$  in  $\text{CHCl}_3$ , the constitution of which is established by its conversion ( $\text{NaI}$  in anhyd.  $\text{COMe}_2$  at  $100^\circ$ ) into styracitol  $\beta\gamma\delta$ -tribenzoate  $\zeta$ -iodohydrin, m.p.  $143\text{--}144^\circ$ ,  $[\alpha]_D^{20} -167^\circ$  in  $\text{CHCl}_3$ . (II) is converted by successive treatments with  $\text{AsF}_5$  in anhyd.  $\text{C}_5\text{H}_5\text{N}$ ,  $\text{Pb}(\text{OAc})_4$  in  $\text{C}_6\text{H}_6$ ,  $\text{NaOMe}$ , and  $\text{NPhMe}\cdot\text{NH}_2$  into  $d$ -fructosephenylmethylhydrazone, m.p.  $156\text{--}158^\circ$ . Oxidation can also be effected with  $\text{BzO}_2\text{H}$ . H. W.

Mixed anhydride of phosphoric and acetic acid. F. Lynen (*Ber.*, 1940, 73, [B], 367—375).— $\text{AcCl}$  (3 mols.) and  $\text{Ag}_3\text{PO}_4$  in  $\text{Et}_2\text{O}$  (in  $\text{CO}_2$ ) give triacetyl phosphate,  $\text{PO}(\text{OAc})_3$ , m.p.  $59\text{--}61^\circ$ , hydrolysed by ice-cold  $\text{H}_2\text{O}$  to  $\text{OH}\cdot\text{PO}(\text{OAc})_2$  (I) and  $\text{AcOH}$ . The rate of hydrolysis of (I) is much slower at pH 7.4 and  $38^\circ$  than in acid medium at  $30^\circ$ .  $\text{CH}_2\text{Ph}\cdot\text{OH}$  and  $\text{P}_2\text{O}_5$  in  $\text{Et}_2\text{O}$  give  $\text{OH}\cdot\text{PO}(\text{O}\cdot\text{CH}_2\text{Ph})_2$  [Ba salt, m.p.  $255\text{--}261^\circ$  (decomp.)]; its  $\text{Ag}_2$  salt, m.p.  $216^\circ$  (decomp.), and  $\text{AcCl}\text{-Et}_2\text{O}$  at room temp., then at  $35^\circ$ , yield  $\text{OAc}\cdot\text{PO}(\text{O}\cdot\text{CH}_2\text{Ph})_2$ , converted by  $\text{H}_2\text{-Pd-C-Et}_2\text{O}$  into  $\text{OAc}\cdot\text{PO}(\text{OH})_2$  (II) (purified through the Ba and  $\text{Ag}_2$  salt). Hydrolysis of (II) to  $\text{H}_3\text{PO}_4 + \text{AcOH}$  in aq.  $\text{NaHCO}_3$  (pH 7.4) at  $38^\circ$  is studied. Absorption spectra of a neutral solution of (II) and of a partly hydrolysed product are given. A. T. P.

General method for synthesis of *tert*-butyl esters. B. Abramovitch, J. C. Shivers, B. E. Hudson, and C. R. Hauser (*J. Amer. Chem. Soc.*, 1943, 65, 986).—Adding  $\text{RCOCl}$  to  $\text{Bu}^t\text{OH} + \text{NPhMe}_2$  in  $\text{Et}_2\text{O}$ , with cooling if necessary, and then boiling gives  $\text{Bu}^t\text{OAc}$  (63—76%),  $\text{EtCO}_2\text{Bu}^t$  (63%),  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Bu}^t$  (70%), b.p.  $73\text{--}74^\circ/25$  mm.,  $\text{Bu}^t$  isobutyrate (71%), b.p.  $127\text{--}128.3^\circ$ , isovalerate (33%), b.p.  $154\text{--}156^\circ$ , and cinnamate (58%), b.p.  $144^\circ/8$  mm. R. S. C.

Petroleum acids. V. Aliphatic acids from Californian petroleum. W. A. Quebedeaux, G. Wash, W. O. Ney, W. W. Crouch, and H. L. Lochte (*J. Amer. Chem. Soc.*, 1943, 65, 767—770; cf. A., 1942, II, 225).—The Me esters of acids from Californian petroleum are distilled to yield 720 fractions, the b.p. and  $n_D$  of which are used for characterisation. Fractions of const. b.p. and low  $n$  yield  $\text{CHMePr}^a\cdot\text{CO}_2\text{H}$ ,  $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $n\text{-C}_5\text{H}_{11}\cdot\text{CO}_2\text{H}$ ,  $\text{CHMeBu}^a\cdot\text{CO}_2\text{H}$ ,  $\text{CHMePr}^a\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $\text{CHMeEt}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ ,  $\text{Pr}^b\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$ ,  $n\text{-C}_6\text{H}_{13}\cdot\text{CO}_2\text{H}$ ,  $n\text{-C}_7\text{H}_{15}\cdot\text{CO}_2\text{H}$ ,  $n\text{-C}_8\text{H}_{17}\cdot\text{CO}_2\text{H}$ , but no  $\text{Bu}^t\text{CO}_2\text{H}$  or  $\text{CHMeEt}\cdot\text{CO}_2\text{H}$  (cf. B., 1939, 1199). R. S. C.

Catalytic reduction by formic acid under pressure. II. Comparison of copper and nickel as catalysts. R. R. Davies and H. H.

Hodgson (*J.C.S.*, 1943, 281—282).—Cu, as catalyst with  $\text{HCO}_2\text{H}$ , promotes non-nuclear reduction,  $\text{PhCHO}$ ,  $\text{BzOH}$ , and  $\text{PhNO}_2$  being reduced to  $\text{CH}_2\text{Ph}\cdot\text{OH}$ , and  $\text{PhMe}$ ,  $\text{C}_6\text{H}_6$ , and  $\text{NH}_2\text{Ph}$  respectively, whilst Ni promotes nuclear reduction,  $\text{NH}_2\text{Ph}$  and  $\text{PhOH}$  giving cyclohexylamine and cyclohexanol. F. R. S.

**Fractional distillation of unsaturated fatty acids. II. Effect of heat on rearrangements produced in unsaturated fatty acid esters.** F. A. Norris, I. I. Rusoff, E. S. Miller, and G. O. Burr (*J. Biol. Chem.*, 1943, 147, 273—280).—Fatty acids containing up to three double linkings are resistant to the heat-treatment of vac. fractional distillation. Rearrangement of isolated to conjugated double linkings occurs in more unsaturated acids, the extent of which depends on the degree of unsaturation, the time, and the temp. Two and three double linking conjugation is observed in heat-treated Me linolenate and the more unsaturated esters of cod-liver oil, respectively. As thermal polymerisation increases, conjugation first increases and then diminishes as the conjugated double linkings undergo a Diels-Alder type of reaction to produce polymers devoid of conjugation. Added reagents and solvents are of importance since a greater concn. of conjugated material is produced by high-temp. hydrolysis than by heat alone. Polymers freed from monomers exhibit only general absorption probably resulting from cyclisation. H. G. R.

**Derivatives from hydrogenated castor oil. II. Glycol esters of  $\lambda$ -hydroxystearic acid.** S. A. Bell and A. Taub (*J. Amer. Pharm. Assoc.*, 1943, 32, 115—118; cf. A., 1942, II, 187).—The following esters are prepared by refluxing the acid in xylene containing  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  with 10 mol.-equivs. of the glycol for the mono- and 2 mol.-equivs. for the di-ester: *ethylene glycol*, m.p. 67—68.5°, *propylene glycol*, m.p. 63—66°, and *trimethylene glycol  $\lambda$ -hydroxystearate*, m.p. 60.5—62°; *ethylene glycol*, m.p. 90—92°, and *trimethylene glycol di- $\lambda$ -hydroxystearate*, m.p. 81.3—82.5°. The physical properties and possible application to ointment bases are described. F. O. H.

**Pyrolysis of lactic acid derivatives. Preparation of allyl and methallyl acrylates.** C. H. Fisher, C. E. Rehberg, and L. T. Smith (*J. Amer. Chem. Soc.*, 1943, 65, 763—767).—Several treatments of lactic acid with  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{OH}$  (I) in presence of acid give 51.5% of *allyl lactate* (II), b.p. 79°/25 mm., but 78% is obtained by dehydrating the acid by boiling with  $\text{C}_6\text{H}_6$  and heating the resulting anhydride with (I). Boiling with  $\text{CH}_2\text{:CMe}\cdot\text{CH}_2\cdot\text{OH}$  and  $\text{C}_6\text{H}_6$  with removal of  $\text{H}_2\text{O}$  gives 64.6% of  $\beta$ -*methylallyl lactate* (III), b.p. 78°/11 mm. Pyrolysis of the *acetates* (prep. by  $\text{Ac}_2\text{O}-\text{H}_3\text{PO}_4$ ), b.p. 98°/20 mm., and 95°/10 mm., of (II) and (III), respectively, at 500—575° gives ~40% of *allyl* (IV), b.p. 122°, and  $\beta$ -*methylallyl acrylate* (V), b.p. 72°/50 mm., respectively. The methylacrylates give higher yields on pyrolysis. Presence of (IV) or (V) leads to less sol., less fusible, harder polymerides, owing to cross-linking. R. S. C.

**Ambrettolide and its isomerides. II.  $\Delta^8$ - and  $\Delta^6$ -isoAmbrettolic acids and their lactones.** C. Collaud (*Helv. Chim. Acta*, 1943, 26, 849—856; cf. A., 1942, II, 392).—Further crystallisation of  $\Delta^6$ -isoambrettolic [ $\alpha$ -hydroxy- $\Delta^6$ -hexadecenoic] acid (I) from  $\text{C}_6\text{H}_6$  during which the temp. is not allowed to fall below 30° raises the m.p. to 77—77.5°. New m.p. of its  $p$ -phenylphenacyl ester is 98—99° and of  $\epsilon\zeta$ -trihydroxyhexadecanoic acid obtained by oxidation with  $\text{KMnO}_4$  102—103°. The *formate* has m.p. 53—54°. (I) is oxidised by  $\text{H}_2\text{O}_2$  to an isomeric  $\epsilon\zeta$ -trihydroxystearic acid, m.p. 114—115°. Crystallisation of the residues left after the isolation of (I) from  $\text{C}_6\text{H}_6$ ,  $\text{EtOAc}$ ,  $\text{C}_6\text{H}_6$ , and light petroleum- $\text{Et}_2\text{O}$  leads to  $\Delta^8$ -isoambrettolic [ $\alpha$ -hydroxy- $\Delta^8$ -hexadecenoic] acid (II), m.p. 61—62° (*formate*, m.p. 43—44°). Ozonisation of (II) followed by reduction of the ozonide and oxidation of the aldehydo-acid gives  $\kappa$ -hydroxyundecanoic and glutaric acid (III) but the presence of very small amounts of adipic (IV) and succinic acid casts some doubt on the homogeneity of (II). Oxidation of (II) by  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  gives  $\delta\epsilon\alpha$ -trihydroxyhexadecanoic acids, m.p. 81—81.5° and 119—119.5° respectively.  $p$ -Phenylphenacyl  $\Delta^8$ -isoambrettolate has m.p. 87—88°.  $\Delta^8$ -isoAmbrettolide, b.p. 143°/2 mm., is hydrolysed to (II). The isoambrettolic acids freely sol. in  $\text{C}_6\text{H}_6$  appear to be mixtures of the geometrical isomerides of (I) and (II) since they yield (III) and (IV) when ozonised. Their separation has not been effected. They have a very marked tendency to pass into estolides, even at room temp. H. W.

**Configurative relationship between optically active methyl- and thiol-succinic acids.** A. Fredga (*Arkiv Kemi, Min., Geol.*, 1942, 15, B, No. 23, 6 pp.).—(+)- $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (I) and (+)- $\text{CO}_2\text{H}\cdot\text{CH}(\text{SH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (II) form a continuous series of solid solutions, and  $r$ -(I) and  $r$ -(II) a limited range, whilst (—)-(I) and (+)-(II) form the racemic type 1:1 compound, m.p. 132.5°. It is concluded that (+)-(I) and (+)-(II) have the same optical configuration (cf. A., 1943, I, 154).  $r$ -(I) has m.p. 112.5° when freshly prepared, rising to m.p. 116° (after sintering) on keeping, indicating the existence of polymorphism. M. H. M. A.

**Fission of thetines of sulphido-acids.** B. Holmberg and E. Schjånberg (*Arkiv Kemi, Min., Geol.*, 1942, 15, A, No. 23, 31 pp.).—The

reaction between  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na}$  and  $\text{CR}'\text{R}''(\text{S}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{Na})_2$  ( $n = 1$  or  $2$ ), or  $\text{SR}'\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{Na}$  (I) ( $n = 1$  or  $2$ ) ( $\text{R}', \text{R}'' = \text{H}$ , alkyl, or aryl), giving, e.g.,  $\text{CHR}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na})\cdot\text{S}^+(\text{CH}_2\cdot\text{CO}_2^-)\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$  (II) +  $\text{NaBr}$ , followed by fission of (II) to  $\text{R}\cdot\text{CHO} + \text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na} + \text{S}(\text{CH}_2\cdot\text{CO}_2^-)_2\text{Na}^+\text{H}^+$ , has been studied by determining  $\text{Br}^-$  and  $\text{H}^+$  produced. No conclusion could be drawn about the mechanism of the reaction or the occurrence of side reactions. The rate of thetination is highest with (I) > mercaptal acids > mercaptol acids, and with derivatives of  $\text{SH}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$  > of  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (III). The effect of changes in  $\text{R}'$  and  $\text{R}''$  is similar in all four series but no regularities are observed. (III) and  $\text{COMePr}^\beta$  with conc.  $\text{HCl}$  at room temp. give *methylisopropylmercaptolacetic acid*, m.p. 100—101°. M. H. M. A.

**Vinylalkylmalonic esters.**—See A., 1943, II, 279.

**Preparation of aldehydes.**—See B., 1943, II, 241.

**Catalytic dehydrogenation of alcohols to aldehydes in presence of air.** R. R. Davies and H. H. Hodgson (*J.C.S.*, 1943, 282—284).—Butyl, dodecyl, and benzyl alcohols are dehydrogenated to aldehydes by Cu-Ag on pumice in presence of air at 300—350° (97, 85, and 76% yields respectively, allowing for alcohol recovered). There is an optimum air:alcohol ratio in each case, the amount of air consumed being  $\ll$  the theoretical for oxidation. A. L.

**Preparation of aldehydes, ketones, and acids by ozone oxidation.** A. L. Henne and P. Hill (*J. Amer. Chem. Soc.*, 1943, 65, 752—754).—Ozonisation of olefines to aldehydes or ketones is best effected in  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ$  (or  $\text{AcOH}$  or  $\text{EtOAc}$  at room temp.); the ozonide is decomposed by dropping the solution into 25—50%  $\text{AcOH}$  containing Zn dust; the product, in  $\text{Et}_2\text{O}$ , is washed with aq. KI to prevent explosions. For prep. of the acid, the solution of the ozonide in  $\text{AcOH}$  is run into  $\text{H}_2\text{O}_2-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ . Prep. of  $\text{Pr}^\beta\cdot[\text{CH}_2]_3\cdot\text{CHO}$  (62%) and  $\text{Pr}^\beta\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$  (67%) from  $\text{Pr}^\beta\cdot[\text{CH}_2]_3\cdot\text{CH}\cdot\text{CH}_2$ , of  $\text{COMeBu}^\alpha$  (60%) from  $\text{CMeBu}^\alpha\cdot\text{CH}_2$ , of  $\text{CO}_2\text{H}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$  (60%) from cyclohexene, of  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$  (50%) from  $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CH}_2$  ( $\text{CH}_2\text{Ph}\cdot\text{CHO}$  could not be obtained), of  $\text{Pr}^\beta\cdot[\text{CH}_2]_5\cdot\text{CHO}$  (66.6%) from  $\text{Pr}^\beta\cdot[\text{CH}_2]_5\cdot\text{CH}\cdot\text{CH}_2$ , and of  $\text{CHMeBu}^\alpha\cdot\text{CH}_2\cdot\text{COMe}$  (68.9%) from  $\text{CHMeBu}^\alpha\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2$  is described. R. S. C.

**Preparation of monomeric glyoxal.**—See B., 1943, II, 241.

**Two different 2:4-dinitrophenylhydrazones of ethyl isopropyl ketone and the 2:4-dinitrophenylhydrazones of other methyl and ethyl ketones.** W. Dirscherl and H. Nahm (*Ber.*, 1940, 73, [B], 448—450).— $\text{COEtPr}^\beta$  and 2:4:1-( $\text{NO}_2$ ) $_2\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$  in 50%  $\text{AcOH}$  give two *Et Pr* $^\beta$  ketone 2:4-dinitrophenylhydrazones, orange-red crystals (I), m.p. 111—113°, and pale yellow crystals (II) which become red at 84—88° and melt at 111—113°. Under  $\text{Et}_2\text{O}$  (I) passes gradually into (II). (I) and (II) are regarded as different modifications, not isomerides. Only one form is observed in the 2:4-dinitrophenylhydrazones of  $\text{COMe}_2$ , m.p. 122—124°,  $\text{COMeEt}$ , m.p. 116—117°,  $\text{COMeBu}^\alpha$ , m.p. 106—109°,  $\text{COMeBu}^\beta$ , m.p. 71.5—72.5°,  $\text{COMeBu}^\gamma$ , m.p. 92—94°,  $\text{COEtPr}^\alpha$ , m.p. 49—151°, *Me isoamyl ketone*, m.p. 93—94°, and  $\text{COPhMe}$ , m.p. 238—240°. H. W.

**Molar refraction and structure of hydroxymethylene ketones.** R. Kaushal (*J. Indian Chem. Soc.*, 1943, 20, 53—55).—*Ethoxymethyleneacetone* (I), b.p. 74—76°/6 mm. (*disemicarbazone*, m.p. 242°; corresponding *anilide*,  $\text{COMe}\cdot\text{CH}\cdot\text{CHNHPh}$ , m.p. 247°), is obtained by the action of  $\text{EtBr}$  in  $\text{EtOH}$  on the product from  $\text{COMe}_2$ ,  $\text{HCO}_2\text{Et}$ , and Na. It gives a red colour with  $\text{FeCl}_3$  which gradually darkens. It is not acid to litmus.  $\gamma$ -*Ethoxymethylenebutan- $\beta$ -one* (II), b.p. 79°/8 mm., is obtained similarly. It gives a faint violet colour with  $\text{FeCl}_3$  which darkens on keeping or warming. After prolonged contact with  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$  it gives a very poor yield of *solid*, m.p. 260°.  $M_D$  of (I) and (II) indicates the constitutions  $\text{COMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{OEt}$  and  $\text{COMe}\cdot\text{CMe}\cdot\text{CH}\cdot\text{OEt}$ , from which the structures of the parent substances are inferred. H. W.

**Preparation of hexadecylamines.**—See B., 1943, II, 241.

**Secondary amino-alcohols.**—See B., 1943, II, 242.

**Ergot alkaloids. V. Synthesis of optically active  $\beta$ -amino-alcohols.** A. Stoll, J. Peyer, and A. Hofmann (*Helv. Chim. Acta*, 1943, 26, 929—943).—Esters of  $r$ - $\alpha$ -bromo-fatty acids are converted into the  $r$ - $\alpha$ -benzylamino-fatty acids, which are smoothly reduced (Bonveault-Blanc) to the cryst.  $\beta$ -benzylamino-alcohols. These are resolved by the appropriate optically active acids and the  $\text{CH}_2\text{Ph}$  group is finally removed by catalytic hydrogenation. The letters *d*- and *l*- are used to express configurative relationships to *d*-malic acid and the signs + and — for sense of rotation. Gradual addition of  $r$ - $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$  (I) in  $\text{EtOH}$  to Na under tetrahydronaphthalene (initially heated to 120°) in such a manner that the temp. remains at ~106—108° leads to *dl*- $\beta$ -benzylaminopropyl alcohol [*dl*-*N*-benzylalaninol] (II), b.p. 155—157°/20 mm., m.p. 70—72° [*hydrochloride*, m.p. 111—113°; *picrate*, m.p. 135—137°; *H oxalate*, m.p. 176—178° (decomp.)], also obtained from (I) by treatment with  $\text{H}_2$  at 180°/200 atm. in dioxan containing Cu chromite. (II) is resolved by *d*-tartaric acid in  $\text{EtOH}-\text{EtOAc}$ , yielding immediately the *H d-tartrate*, m.p. 94—96°, of *d*-(—)- $\beta$ -benzylaminopropyl

*alcohol* (III), m.p. 47—49°,  $[\alpha]_D^{25} - 44.25^\circ$  in EtOH [hydrochloride, m.p. 136—138°,  $[\alpha]_D^{25} - 14.75^\circ$  in H<sub>2</sub>O; *H oxalate*, m.p. 187—189° (decomp.); *picrate*, m.p. 73—75°]. The basic residue from the isolation of (III) is cryst. from cyclohexane and then converted into the *H oxalate*, from which *l*(+)- $\beta$ -benzylaminopropyl alcohol (IV),  $[\alpha]_D^{25} + 44^\circ$  in EtOH, is derived. Hydrogenation (Pd sponge) of (IV) and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in aq. EtOH affords the *oxalate*, m.p. 171° (corr.),  $[\alpha]_D^{25} + 18.8^\circ$  in H<sub>2</sub>O, of *l*(+)- $\beta$ -aminopropyl alcohol, b.p. 72—73°/11 mm.,  $[\alpha]_D^{25} + 15.8^\circ$ . *d*(-)- $\beta$ -Aminopropyl alcohol (*oxalate*,  $[\alpha]_D^{25} - 18.8^\circ$  in H<sub>2</sub>O) is identical with the product derived from ergobasine. Gradual addition of Na to a boiling solution of *r*-CH<sub>2</sub>Ph·NH·CH<sub>2</sub>Et·CO<sub>2</sub>Et in abs. EtOH leads to *dl*- $\beta$ -benzylaminobutanol (V), b.p. 155—157°/14 mm., m.p. 58—60° (hydrochloride, m.p. 127—129°; *picrate*, m.p. 144—146°). (V) is resolved by successive use of *d*(-)- and *l*(+)-OH·CHPh·CO<sub>2</sub>H in EtOAc. The *d*(-)-*mandelate*, m.p. 111—113°, of (-)- $\beta$ -benzylaminobutanol, m.p. 76—78°,  $[\alpha]_D^{25} - 25.0^\circ$  in EtOH (hydrochloride, m.p. 141—143°; *picrate*, m.p. 111—113°), and (+)- $\beta$ -benzylaminobutanol,  $[\alpha]_D^{25} + 25.5^\circ$  in EtOH, are isolated. Hydrogenation of the alcohols leads to (+)- $\beta$ -aminobutanol, b.p. 80°/11 mm.,  $[\alpha]_D^{25} + 9.8^\circ$  [*oxalate*, m.p. 190—192° (corr.),  $[\alpha]_D^{25} + 11.3^\circ$  in H<sub>2</sub>O], and (-)- $\beta$ -aminobutanol,  $[\alpha]_D^{25} - 11.3^\circ$ . *r*-CH<sub>2</sub>Ph·NH·CMeEt·CO<sub>2</sub>Et is converted into *r*- $\beta$ -benzylamino- $\beta$ -methyl-*n*-butyl alcohol, b.p. 146—148°/8 mm. (hydrochloride, m.p. 152—154°; *picrate*, m.p. 131—133°). *dl*-CH<sub>2</sub>Ph·NH·CHBu·CO<sub>2</sub>Et readily gives *dl*- $\beta$ -benzylamino- $\delta$ -methyl-*n*-amyl alcohol, b.p. 170—172°/16 mm., m.p. 61—63° (hydrochloride, m.p. 151—153°; *picrate*, m.p. 152—154°). This is resolved by *d*-dibenzoyltartaric acid in 60% EtOH, whereby there is separation of the *H d*-dibenzoyltartrate, m.p. 169—171° somewhat dependent on the rate of heating, of *l*(+)- $\beta$ -benzylamino- $\delta$ -methyl-*n*-amyl alcohol [*l*(+)-*N*-benzyl-leucinol] (VI), m.p. 77—79°,  $[\alpha]_D^{25} + 30.75^\circ$  in EtOH (hydrochloride, m.p. 160—162°; *picrate*, m.p. 121—123°). *d*(-)- $\beta$ -Benzylamino- $\delta$ -methyl-*n*-amyl alcohol,  $[\alpha]_D^{25} - 30.25^\circ$  in EtOH, is isolated from the bases left after separation of (VI) by use of (+)-*o*-nitromandelic acid and 50% EtOH. *d*(-)- $\beta$ -Amino- $\delta$ -methyl-*n*-amyl alcohol, b.p. 98—99°/11 mm. [*oxalate*, m.p. 216° (corr.),  $[\alpha]_D^{25} - 7.0^\circ$  in H<sub>2</sub>O], and its *l*(+)-*antipode*, b.p. 98—99°/11 mm. [*oxalate*, m.p. 216° (corr.),  $[\alpha]_D^{25} + 7.2^\circ$  in H<sub>2</sub>O], are obtained in the usual manner. CH<sub>2</sub>Ph·CH(NH·CH<sub>2</sub>Ph)·CO<sub>2</sub>Et, b.p. 198—200°/6 mm., is reduced to  $\beta$ -benzylamino- $\gamma$ -phenyl-*n*-propyl alcohol [*dl*-phenyl-*N*-benzylalaninol], b.p. 198—200°/5 mm., m.p. 69—71° (hydrochloride, m.p. 147—149°; *picrate*, m.p. 166—168°).

H. W.

**Amino-acids. I. Glycine.** J. H. Billman and E. E. Parker (*J. Amer. Chem. Soc.*, 1943, **65**, 761—762).—*o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>N·[CH<sub>2</sub>]<sub>2</sub>·OH {prep. from *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O and NH<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·OH at 175° in 99% yield} with hot K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-AcOH-H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> gives 89—93% of *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>N·CH<sub>2</sub>·CO<sub>2</sub>H, hydrolysed by boiling 18% HCl to NH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>H·HCl (79—85%), which with warm C<sub>6</sub>H<sub>5</sub>N and then MeOH gives 65—73% of glycine.

R. S. C.

**Amino-acids and their derivatives. III. Synthesis of  $\alpha$ -aminodi-*n*-propylacetic acid.** Y. T. Huang, K. H. Lin, and L. Li (*J. Chinese Chem. Soc.*, 1941, **8**, 81—91).—CN·CPr<sub>2</sub>·CO<sub>2</sub>Et with conc. H<sub>2</sub>SO<sub>4</sub> yields Et di-*n*-propylmalonamate (free acid, m.p. 148—150°), which with Br in CHCl<sub>3</sub> gives the *N*-Br-compound, m.p. 47—48°, hydrolysed (10% NaOH, 70—80°) to NN'-bis(carbethoxydi-*n*-propylmethyl)-carbamide (I), m.p. 111—112°, or (10% NaOH, 20—30°) to (II) and (chiefly) the Et ester, b.p. 80—81°/6—7 mm. (hydrochloride, m.p. 94—95°; *phenylureide*, m.p. 110.5—111.5°), of  $\alpha$ -amino- $\alpha$ -propyl-*n*-valeric acid (II), m.p. 312° (decomp.) (bath preheated to 290°) [*hydrochloride*, m.p. 295—296° (decomp.) (bath preheated to 280°); *ureide*, m.p. 240° (decomp.) (bath preheated to 195°); CH<sub>2</sub>Cl·CO derivative, m.p. 216° (bath preheated to 200°)]. (I) is hydrolysed by HI (½ hr.) to NN'-bis(carboxydi-*n*-propylmethyl)-carbamide, m.p. 272° (bath preheated to 260°), or (4½ hr.) to (II).

A. Li.

**Amino-acids and their derivatives. IV. Synthesis of  $\alpha$ -aminodi-*n*-butylacetic acid and  $\alpha$ -aminodiisobutylacetic acid.** Y. T. Huang, K. H. Lin, L. Li, and M. C. Lin (*J. Chinese Chem. Soc.*, 1941, **8**, 201—217).—CN·CBu <sup>$\alpha$</sup> ·CO<sub>2</sub>Et or CN·CBu <sup>$\beta$</sup> ·CO<sub>2</sub>Et (from CN·CH<sub>2</sub>·CO<sub>2</sub>Et, AlkBr, and NaOEt in EtOH) with conc. H<sub>2</sub>SO<sub>4</sub> at 100° yield respectively Et di-*n*-, m.p. 75—76° [free acid, m.p. 148° (decomp.)], and -iso-butylmalonamate, new m.p. 79.5—80.5° [free acid, new m.p. 159° (decomp.)], which with Br in CHCl<sub>3</sub> at -15° give the crude *N*-Br-compounds (I) and (II) respectively, hydrolysed to carbethoxydi-*n*- (III), b.p. 107°/4.5 mm., and -iso-butylmethylcarbamide (IV), b.p. 95°/3.5 mm. (III) yields with NH<sub>2</sub>Ph at room temp., then at 45—50°, Et  $\alpha$ -phenylureido- $\alpha$ -butyl-*n*-hexoate (V), m.p. 151—152° (bath preheated to 140°), with NH<sub>2</sub>·CPr<sub>2</sub>·CO<sub>2</sub>H in *N*-NaOH at room temp., then at 70—75°, *N*-(carboxydi-*n*-propylmethyl)-*N'*-(carbethoxydi-*n*-butylmethyl)-carbamide, m.p. 152—153° (decomp.) (bath preheated to 140°), and with conc. HCl at room temp., then at 100°, Et  $\alpha$ -amino- $\alpha$ -butyl-*n*-hexoate hydrochloride, m.p. 102—103° [also obtained from (I) and 10% NaOH at 25—30°], with NN'-bis(carbethoxydi-*n*-butylmethyl)-carbamide (VI), m.p. 75—78°, hydrolysed (HI at 150—170° for ½ hr.) to the free acid, m.p. 262—263° (bath preheated to 250°) [the free ester from which with PhNCO gives (V)], further hydrolysed (boiling 20% HCl) to  $\alpha$ -amino- $\alpha$ -*n*-butyl-*n*-hexoic acid, m.p. 303° (bath preheated

to 290°) [also obtained from (VI) and HI at 150—170° for 6 hr.], [*phenylureide*, m.p. 182—183° (decomp.) (bath preheated to 170°);  $\alpha$ -CH<sub>2</sub>Cl·CO derivative, m.p. 192—193°], which with (III) at 70—80°, then 85—90°, yields *N*-(carboxydi-*n*-butylmethyl)-*N'*-(carbethoxydi-*n*-butylmethyl)-carbamide, m.p. 148—149° (froth) (bath preheated to 135°), esterified (Ag salt with EtI) to (VI). (IV) is hydrolysed (fuming HCl at 100°, 1 hr.) to Et  $\alpha$ -amino- $\beta$ -methyl- $\alpha$ -isobutylvalerate hydrochloride, m.p. 188—192°, which with aq. KCNO gives Et  $\alpha$ -ureido- $\beta$ -methyl- $\alpha$ -isobutylvalerate, m.p. 159.5—160.5° [also obtained from (III) and aq. NH<sub>3</sub> at room temp., then 50—55°, then 60—65°], and is further hydrolysed (48 hr.) to the hydrochloride, m.p. 261—264° (decomp.) (bath preheated to 250°), of  $\alpha$ -amino- $\beta$ -methyl- $\alpha$ -isobutylvaleric acid, m.p. 279° (bath preheated to 270°) [*phenylureide*, m.p. 204° (decomp.) (bath preheated to 195°); CH<sub>2</sub>Cl·CO-derivative, m.p. 207° (bath preheated to 195°)].

A. Li.

**Improved preparation of nitrosomethylcarbamide.** F. Arndt, L. Loewe, and S. Avan (*Ber.*, 1940, **73**, [B], 606—608).—CO(NH<sub>2</sub>)<sub>2</sub> with aq. NH<sub>2</sub>Me·HCl or 33% aq. NH<sub>3</sub>·Me<sub>2</sub>SO<sub>4</sub>, followed by NaNO<sub>2</sub>-ice-H<sub>2</sub>SO<sub>4</sub> at -10°, gives NO·NMe·CO·NH<sub>2</sub>.

A. T. P.

**Hexafluoroazomethane (dicyanohexafluoride).** O. Ruff and W. Willenberg (*Ber.*, 1940, **73**, [B], 724—729; cf. A., 1936, 597).—CF<sub>3</sub>·N<sub>2</sub>·CF<sub>3</sub>, m.p. -133°, b.p. -31.6°/760 mm., is obtained from CNI and IF<sub>5</sub> at 125—145°; hexafluorodimethylamine, NH(CF<sub>3</sub>)<sub>2</sub>, m.p. -130°, b.p. -6.2°/760 mm., is also formed. Various chemical and physical properties of the substances are described.

A. T. P.

## II.—SUGARS AND GLUCOSIDES.

**Derivatives of the aldehydrol form of sugars. V. Rotatory power.** M. L. Wolfrom and R. L. Brown (*J. Amer. Chem. Soc.*, 1943, **65**, 951—953; cf. A., 1941, II, 242).—*aldehydo-d*-Arabinose tetra-acetate with AcCl + ZnCl<sub>2</sub> in AcOH (+ a little Ac<sub>2</sub>O) at 20—25° gives  $\alpha$ -, m.p. 109—110°,  $[\alpha]_D^{20} + 97.1^\circ$  in CHCl<sub>3</sub>, and  $\beta$ -1-chloro-*aldehydo-d*-arabinose penta-acetate, m.p. 67.5—68.5°,  $[\alpha]_D^{20} - 29.5^\circ$  in CHCl<sub>3</sub>.  $\alpha$ -, m.p. 129—130°,  $[\alpha]_D^{25} + 135.7^\circ$  in CHCl<sub>3</sub>, and  $\beta$ -Bromo-*aldehydo-d*-arabinose penta-acetate, m.p. 63—64°,  $[\alpha]_D^{20} - 71.3^\circ$  in CHCl<sub>3</sub>, and  $\alpha$ -, m.p. 142.5—143°,  $[\alpha]_D^{25} + 98.0^\circ$  in CHCl<sub>3</sub>, and  $\beta$ -1-bromo-*aldehydo-d*-galactose hexa-acetate, m.p. 178—180°,  $[\alpha]_D^{25} - 75^\circ$  in CHCl<sub>3</sub>, are similarly prepared. Hudson's isorotation rules are valid in these series.

R. S. C.

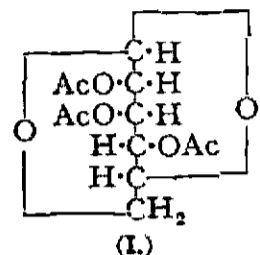
**Production of *d*-ribose from calcium *d*-altronate.**—See B., 1943, II, 242.

**Partly-methylated glucose.** K. Freudenberg and E. Plankenhorn (*Ber.*, 1940, **73**, [B], 621—631).—4 : 6-Benzylidene- $\alpha$ -methylglucoside and CH<sub>2</sub>PhCl-KOH at 100° give the 2 : 3-(CH<sub>2</sub>Ph)<sub>2</sub> derivative, m.p. 99°,  $[\alpha]_D^{20} + 23.5^\circ$  in COMe<sub>2</sub>, hydrolysed by 1% HCl in EtOH to 2 : 3-dibenzyl- $\alpha$ -methylglucoside, m.p. 79—80°,  $[\alpha]_D^{20} + 88.7^\circ$  in COMe<sub>2</sub>, which with Me<sub>2</sub>SO<sub>4</sub>-aq. KOH-COMe<sub>2</sub> at 50° yields 2 : 3-di-benzyl-4 : 6-dimethyl- $\alpha$ -methylglucoside, b.p. 200—210°/0.45 mm.,  $[\alpha]_D^{20} + 97.9^\circ$  in COMe<sub>2</sub>, converted by H<sub>2</sub>-Pd oxide-MeOH into 4 : 6-dimethyl- $\alpha$ -methylglucoside, b.p. 120°/0.005 mm.,  $[\alpha]_D^{20} + 155.3^\circ$  to 157.3° in CHCl<sub>3</sub> [2 : 3-di-*p*-nitrobenzoate, m.p. 114° (softens from 110°),  $[\alpha]_D^{20} + 203^\circ$  in COMe<sub>2</sub>, and 2 : 3-di-*p*-benzeneazobenzoate, m.p. 120°,  $[\alpha]_D^{20} + 405^\circ$  in COMe<sub>2</sub>]. The derived 4 : 6-dimethylglucose has m.p. 156—158°; in MeOH-HCl, mutarotation occurs, e.g.,  $[\alpha]_D + 85.2^\circ \rightarrow + 61.3^\circ$ . 3-Benzyl-5 : 6-dimethyl-1 : 2-isopropylideneglucose, b.p. 160°/0.2 mm.,  $[\alpha]_D^{20} - 15.8^\circ$  in COMe<sub>2</sub>, obtained from the 5 : 6-diacetate and Me<sub>2</sub>SO<sub>4</sub>-aq. NaOH in COMe<sub>2</sub>, is converted by H<sub>2</sub>-Pd-MeOH into 5 : 6-dimethyl-1 : 2-isopropylideneglucose, b.p. 112°/0.4 mm.,  $[\alpha]_D^{20} - 5.2^\circ$  in MeOH, and thence (HCl) 5 : 6-dimethylglucofuranose, a syrup,  $[\alpha]_D^{20} + 3.7^\circ$  in COMe<sub>2</sub> [1 : 2 : 3-tri-*p*-nitrobenzoate, m.p. 115—120° (softens at 90°),  $[\alpha]_D^{20} + 90.0^\circ$  in COMe<sub>2</sub>, and -tri-*p*-benzeneazobenzoate, m.p. 192° (softens at 188°),  $[\alpha]_D^{20} + 13.3^\circ$  in COMe<sub>2</sub>]. Hexamethylmaltose anhydride, m.p. 66°,  $[\alpha]_D^{20} + 74^\circ$  in CHCl<sub>3</sub> (from maltose anhydride, K, liquid NH<sub>3</sub>, and MeI), is hydrolysed by 5% HCl at 100° (bath) to tetramethylglucose, and also (after treatment with *p*-Ph·N·N·C<sub>6</sub>H<sub>4</sub>·COCl) yields 2 : 3-dimethylglucose tri-*p*-benzeneazobenzoate, m.p. 209°,  $[\alpha]_D^{20} + 100^\circ$  in CHCl<sub>3</sub>, and a second form, m.p. 189° (softens at 170°). 2 : 3-Dimethyl- $\alpha$ -methylglucoside and CH<sub>2</sub>PhCl-KOH at 100° (bath) give the 4 : 6-(CH<sub>2</sub>Ph)<sub>2</sub> compound, b.p. 195—200°/0.3 mm.,  $[\alpha]_D^{20} + 121.9^\circ$  in COMe<sub>2</sub>; methylglucoside 2 : 3-dibenzoate 4 : 6-diacetate, m.p. 125°,  $[\alpha]_D^{20} + 155^\circ$  in COMe<sub>2</sub>, is obtained from  $\alpha$ -methylglucoside 2 : 3-dibenzoate. 6-Triphenylmethyl-2 : 3-dimethyl- $\alpha$ -methylglucoside and BzCl-C<sub>6</sub>H<sub>5</sub>N afford the 4-benzoate, m.p. 133°,  $[\alpha]_D^{20} + 56^\circ$  in COMe<sub>2</sub> (cf. Robertson, A., 1933, 937); similarly prepared is the 4-3' : 5'-dinitrobenzoate, m.p. 175°,  $[\alpha]_D^{20} + 45.7^\circ$  in COMe<sub>2</sub>, which with HBr-AcOH yields 2 : 3-dimethyl- $\alpha$ -methylglucoside 4-3' : 5'-dinitrobenzoate, m.p. 126°,  $[\alpha]_D^{20} + 57.5^\circ$  in COMe<sub>2</sub>. Methylation yields 2 : 3 : 6-trimethyl- $\alpha$ -methylglucoside 4-3' : 5'-dinitrobenzoate, m.p. 147°,  $[\alpha]_D^{20} + 56.3^\circ$  in COMe<sub>2</sub> (corresponding  $\beta$ -glucoside, m.p. 146°,  $[\alpha]_D^{20} - 58.2^\circ$  in COMe<sub>2</sub>, also obtained by dinitrobenzoylation of the respective glucoside); 2 : 3 : 6-trimethyl- $\alpha$ -methylglucoside has  $[\alpha]_D^{20} + 149^\circ$  in MeOH. The following derivatives are prepared, using *p*-PhN<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·COCl-C<sub>6</sub>H<sub>5</sub>N at 40° : 2 : 3 : 4 : 6-tetramethylglucose 1-*p*-benzeneazobenzoate, m.p. 116°,  $[\alpha]_D^{20} - 7^\circ$  in COMe<sub>2</sub>; 2 : 3 : 6-trimethyl- $\beta$ -methylglucoside

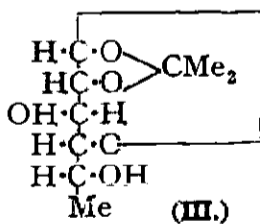
4-*p*-benzeneazobenzoate, m.p. 95—96°,  $[\alpha]_{D}^{20} - 66.2^\circ$  in  $\text{COMe}_2$ ; 2:3:6-trimethylglucose 1:4-di-*p*-benzeneazobenzoate, m.p. 172°,  $[\alpha]_{D}^{20} + 12.6^\circ$  in  $\text{COMe}_2$ ; 2:3:4-trimethyl- $\beta$ -methylglucoside 6-*p*-benzeneazobenzoate, m.p. 122°,  $[\alpha]_{D}^{20} - 7.6^\circ$  to  $-9.3^\circ$  ( $\pm 3.3^\circ$ ) in  $\text{COMe}_2$ ; 2:3:4-trimethylglucose 1:6-di-*p*-benzeneazobenzoate,  $[\alpha]_{D}^{20} - 16.3^\circ$  in  $\text{COMe}_2$ ; 2:4:6-trimethylglucose 1:3-di-*p*-benzeneazobenzoate, m.p. 115—120°,  $[\alpha]_{D}^{20} + 190^\circ$  in  $\text{COMe}_2$ ; 2:3-dimethyl- $\alpha$ -methylglucoside 4:6-di-*p*-benzeneazobenzoate, m.p. 143—144°,  $[\alpha]_{D}^{20} + 260.5^\circ$  in  $\text{CHCl}_3$ ; 4:6-dimethylglucose 1:2:3-tri-*p*-benzeneazobenzoate, m.p. 145°,  $[\alpha]_{D}^{20} + 551^\circ$  in  $\text{CHCl}_3$ ; 3-methyl-, m.p. 220°,  $[\alpha]_{D}^{20} + 163^\circ$  ( $\pm 6^\circ$ ) in  $\text{CHCl}_3$ , and 3-benzyl-glucose 1:2:4:6-tetra-*p*-benzeneazobenzoate, m.p. 246°,  $[\alpha]_{D}^{20} - 48^\circ$  ( $\pm 20^\circ$ ) in  $\text{CHCl}_3$ ; diisopropylideneglucose 3-*p*-benzeneazobenzoate, m.p. 110—111°,  $[\alpha]_{D}^{20} - 56^\circ$  in  $\text{COMe}_2$ .

A. T. P.

**Lævo-mannosan** [ $\beta$ -mannosan]. G. Zemplén, A. Gerecs, and T. Valatin (*Ber.*, 1940, **73**, [B], 575—580).— $\alpha$ -Acetobromo-*D*-mannose and  $\text{NMe}_3$  (method: cf. Micheel, A., 1930, 455) yield a product which affords, after acetylation with  $\text{Ac}_2\text{O}$ - $\text{NaOAc}$  at 100° (bath),  $\beta$ -mannosan 2:3:4-triacetate (I), m.p. 86°,  $[\alpha]_{D}^{20} - 103.6^\circ$  in  $\text{H}_2\text{O}$ ,  $-100.2^\circ$  in  $\text{MeOH}$ ,  $-124.1^\circ$  in  $\text{CHCl}_3$ , converted by  $\text{NaOMe}$ - $\text{MeOH}$  into  $\beta$ -mannosan (II),  $\text{C}_6\text{H}_{10}\text{O}_5$ ,  $[\alpha]_{D}^{20} - 115.4^\circ$  in  $\text{H}_2\text{O}$ , or by 1%  $\text{HCl}$  in  $\text{MeOH}$  into  $\alpha$ -methyl-*D*-mannoside, m.p. 194°,  $[\alpha]_{D}^{20} + 82.5^\circ$  in  $\text{H}_2\text{O}$ . Methylation ( $\text{Me}_2\text{SO}_4$ -aq.  $\text{NaOH}$ ) of (II) affords 2:3:4-trimethyl- $\beta$ -mannosan, m.p. 52°,  $[\alpha]_{D}^{20} - 70.7^\circ$  in  $\text{COMe}_2$ , converted by aq.  $\text{HCl}$  into 2:3:4-trimethylmannose,  $[\alpha]_{D}^{20} - 5^\circ$  in  $\text{H}_2\text{O}$ , which with  $\text{Ac}_2\text{O}$ - $\text{NaOAc}$  gives the 1:6-diacetate,  $[\alpha]_{D}^{20} + 2.24^\circ$  in  $\text{EtOH}$ , and with  $\text{CPh}_3\text{Cl}$ - $\text{C}_5\text{H}_5\text{N}$  yields 6-triphenylmethyl-2:3:4-trimethyl-*D*-mannose. A. T. P.



**Attempted syntheses of glucosides and disaccharides.** K. Freudenberg, H. Eich, C. Knoevenagel, and W. Westphal (*Ber.*, 1940, **73**, [B], 441—447).—Diisopropylideneglucose (I) is converted by Na or K in liquid  $\text{NH}_3$  into the Na and K derivatives, the former of which with  $\text{TiNO}_3$  yields the Ti compound. These react with  $\text{CH}_2\text{PhCl}$  or MeI with increasing readiness in the sequence Na, K, Ti but could not be caused to react with acetohalogenoglucose or 1-chlorodiisopropylidenemannose. (I) and  $\text{COCl}_2$  in quinoline-PhMe yield diisopropylideneglucosyl chloroformate (II), b.p. 120°/0.2 mm.,  $[\alpha]_{D}^{20} - 40.1^\circ$  in  $\text{CHCl}_3$ , which on exposure to moist air passes into isopropylideneglucosyl 5:6-carbonate, decomp. 219—222°,  $[\alpha]_{D}^{20} - 33.7^\circ$  in  $\text{COMe}_2$ ,  $-21.1^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , converted by heat into isopropylidene-5:6-anhydroglucose, m.p. 56—57°. 1:2-isopropylideneglucosyl 5:6-carbonate 3-acetate has m.p. 128—129°,  $[\alpha]_{D}^{20} - 43.2^\circ$  in  $\text{CHCl}_3$ . (II) and  $\beta$ -glucose 2:3:4:6-tetra-acetate in  $\text{C}_6\text{H}_6$ - $\text{C}_5\text{H}_5\text{N}$  afford diisopropylideneglucosyl  $\beta$ -2:3:4:6-tetra-acetylglucosyl carbonate, m.p. 108°,  $[\alpha]_{D}^{20} - 23.1^\circ$  in  $\text{MeOH}$ ,  $-22.6^\circ$  in  $\text{CHCl}_3$ . Diisopropylideneglucosyl diisopropylidenemannosyl carbonate, m.p. 132°,  $[\alpha]_{D}^{20} + 16.4^\circ$  in  $\text{COMe}_2$ , guaiacetyl tetra-acetylglucosyl carbonate, m.p. 146—147°, and menthyl tetra-acetylglucosyl carbonate, m.p. 151°, are described. Elimination of  $\text{CO}_2$  from these esters with formation of disaccharide derivatives or glucosides could not be effected. Menthyl tetra-acetylglucosyl sulphite, m.p. 104—105°,  $[\alpha]_{D}^{20} - 62.9^\circ$  in  $\text{COMe}_2$ , from menthol, glucose tetra-acetate, and  $\text{SOCl}_2$  in  $\text{CHCl}_3$ - $\text{C}_5\text{H}_5\text{N}$ , passes when heated with  $\text{BaCO}_3$  at 144° into  $\beta$ -menthylglucoside tetra-acetate, m.p. 129°, in poor yield; *n*-propyl-tetra-acetylglucosyl sulphite, m.p. 74°,  $[\alpha]_{D}^{20} + 104^\circ$  in  $\text{COMe}_2$ , does not lose  $\text{SO}_3$  when heated. 1:2-isopropylidene-5:6-anhydroglucose is hydrogenated (Pd sponge in  $\text{EtOAc}$ ) to 1:2-isopropylideneglucosylmethylolose (III), m.p. 95°,  $[\alpha]_{D}^{20} - 26.3^\circ$  in  $\text{CHCl}_3$  (diacetate, m.p. 96°,  $[\alpha]_{D}^{20} + 23.0^\circ$  in  $\text{CHCl}_3$ ), which condenses with acetobromoglucose in  $\text{CHCl}_3$  containing  $\text{Ag}_2\text{CO}_3$  to 5-tetra-acetylglucosido-1:2-isopropylideneglucosylmethylolose, m.p. 141°,  $[\alpha]_{D}^{20} - 11.0^\circ$  in  $\text{CHCl}_3$  (acetate, m.p. 128°,  $[\alpha]_{D}^{20} - 46^\circ$  in  $\text{CHCl}_3$ ). Acetylglucosamine and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  in boiling  $\text{MeOH}$  afford *N*-acetyl- $\alpha$ -methylglucosaminide, m.p.  $\sim 189^\circ$ . H. W.



**Crystalline  $\beta$ -D-glucosyl-L-talo-octose** (syn. *D*-gluco- $\alpha$ -L-talo-octose). (Miss) A. T. Merrill, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 994—995).—Na-Hg reduces *D*-gluco-L-gala- and -L-talo-octonolactones to *D*-gluco-L-gala- (I) and -L-talo-octose (II), m.p. 117—118° (corr.),  $[\alpha]_{D}^{20} \sim -32^\circ \rightarrow -6.5^\circ$  (complex mutarotation; unimol. coeff. decrease during reaction), which give the same osazone. (I) and (II) give benziminazole derivatives,  $[\alpha]_{D}^{20} - 44.7^\circ$  and  $+18.6^\circ$ , respectively, in 0.1N-HCl, and with  $\text{H}_2$ -Raney Ni give *D*-gluco-L-gala-, m.p. 153—154°,  $[\alpha]_{D}^{20} + 2.4^\circ$  in  $\text{H}_2\text{O}$  (octa-acetate, m.p. 141°,  $[\alpha]_{D}^{20} + 20.7^\circ$  in  $\text{CHCl}_3$ ), and -L-talo-octitol, m.p. 161°,  $[\alpha]_{D}^{20} - 0.8^\circ$  in  $\text{H}_2\text{O}$  (octa-acetate, m.p. 102°,  $[\alpha]_{D}^{20} + 17.4^\circ$  in  $\text{CHCl}_3$ ).  $[\alpha]$  are as expected. R. S. C.

**Synthesis of  $\beta$ -D-glucosides.** B. Helferich and J. Goerdeler (*Ber.*, 1940, **73**, [B], 532—542).—The course of the reaction between acetobromoglucose (I) and  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{OH}$  (II) or  $\text{CH}_2\text{:CH}\cdot\text{CHMe}\cdot\text{OH}$  (III) in  $\text{CHCl}_3$  containing  $\text{Ag}_2\text{O}$  is followed by distillation of the liquid after fixed intervals and determination of (II) or (III) in the distillate iodometrically. Without further addition the yield of glucoside attains 91% from (I) and (II) or 82% from (I) and (III)

with a mol. ratio alcohol:(I) = 1:3. In both cases addition of  $\text{CaCl}_2$  is unfavourable probably because of its compound formation with (II) or (III); simultaneous addition of I is impracticable. Drierite with the reactants in mol. ratio 1:1 increases the yield to 80% and 63% respectively with (II) and (III) against 53% and 39% for the unaided change. The change is usually complete in 30 min.; only in presence of  $\text{CaCl}_2$  is longer time advisable.  $\text{Hg}_2\text{O}$ ,  $\text{Cu}_2\text{O}$ , and  $\text{Ti}_2\text{O}_3$  do not cause glucoside formation.  $\beta$ -Dibromopropyl- $\beta$ -D-glucoside (IV), m.p. 101.5—103°,  $[\alpha]_{D}^{20} - 3.8^\circ$  in  $\text{H}_2\text{O}$ , is obtained by cautious de-acetylation ( $\text{NaOMe}$  in boiling  $\text{MeOH}$ ) of its tetra-acetate. Its quant. enzymic fission leads to (–)- $\beta$ -D-bromopropanol but its optical homogeneity is not established. Fehling's solution is not reduced by glucose in presence of (IV) or bromoallylglucoside (V). Probably (V) loses  $\text{HBr}$  to give an acetylenyl compound which combines with  $\text{Cu}^+$  formed by the glucose; the resulting compound is rendered  $\text{H}_2\text{O}$ -sol. by adventitious sugar. The free  $\alpha\beta$ -dibromohydrin gives epibromohydrin, thus explaining the reaction. *dl*- $\text{CH}_2\text{:CH}\cdot\text{CHMe}\cdot\text{OH}$  affords  $\Delta\beta$ -butenyl- $\beta$ -D-glucoside tetra-acetate, m.p. 96—97° after softening,  $[\alpha]_{D}^{18} - 19.5^\circ$  in  $\text{CHCl}_3$ , de-acetylated by  $\text{Ba}(\text{OMe})_2$  to the free glucoside, m.p. 101—103°,  $[\alpha]_{D}^{18} - 38.2^\circ$  in  $\text{H}_2\text{O}$ ; this is hydrolysed by almond emulsin to an alcohol,  $\alpha_D - 0.04^\circ$  ( $l = 1$ ). Ozonisation of allylglucoside tetra-acetate in  $\text{AcOH}$  followed by reductive hydrolysis ( $\text{H}_2$ -Pd- $\text{BaSO}_4$ - $\text{AcOH}$ ) gives glycollaldehyde- $\beta$ -D-glucoside tetra-acetate semicarbazone, m.p. 202—205° (decomp.),  $[\alpha]_{D}^{20} - 16.1^\circ$  in  $\text{AcOH}$ , de-acetylated to glycollaldehyde- $\beta$ -D-glucoside semicarbazone, m.p. 168—169°,  $[\alpha]_{D}^{20} - 31.8^\circ$  in  $\text{H}_2\text{O}$ ; this is converted by  $\text{PhCHO}$  into the glassy free glucoside. M.p. are corr. H. W.

**Sorbitylglucosides and  $\beta$ -D-glucosyl-pentamethylsorbitol.** M. L. Wolfrom and T. S. Gardner (*J. Amer. Chem. Soc.*, 1943, **65**, 750—752).—Gentiobiose +  $\text{MeOH}$  with  $\text{H}_2$ -Ni-kieselguhr in  $\text{H}_2\text{O}$  at 150°/163 atm. gives gentiobitol [6- $\beta$ -D-glucosido-1-sorbitol] (80%), amorphous,  $[\alpha]_{D}^{25} - 24^\circ$  in  $\text{H}_2\text{O}$  (nona-acetate, m.p. 88—89.5°,  $[\alpha]_{D}^{26} - 11^\circ$  in  $\text{CHCl}_3$ ), which does not reduce Fehling's solution and is hydrolysed by boiling 5%  $\text{HCl}$  to *l*-sorbitol [(CHPh)<sub>3</sub> derivative] and *D*-glucose ( $\text{Et}_2$  mercaptal). Treating lactitol twice with  $\text{Me}_2\text{SO}_4$ - $\text{NaOH}$  and adding the product followed by MeI to Na in  $\text{Et}_2\text{O}$  gives lactitol  $\text{Me}_3$  ether ( $\sim 80\%$ ), a syrup,  $[\alpha]_{D}^{25} - 13.5^\circ$  in  $\text{CHCl}_3$ . Maltitol  $\text{Me}_3$  ether, a syrup,  $[\alpha]_{D}^{24} + 89^\circ$  in  $\text{CHCl}_3$ , is similarly prepared ( $\sim 80\%$ ). aldehydo-*D*-Glucose  $\text{Me}_3$  ether with  $\text{H}_2$ -Raney Ni in  $\text{EtOH}$  at 175°/163 atm. gives *l*-sorbitol  $\beta$ -D-glucosyl- $\text{Me}_3$  ether, a syrup,  $[\alpha]_{D}^{24} + 47^\circ$  in  $\text{CHCl}_3$  (1-*N*- $\alpha$ -naphthylcarbamate, m.p. 75—76°,  $[\alpha]_{D}^{22} - 5^\circ$  in  $\text{CHCl}_3$ ). R. S. C.

**Saponin of Chinese drug "san-chi."** I. C. F. Hsu (*J. Chinese Chem. Soc.*, 1941, **8**, 15—20).—Saponin A,  $\text{C}_{48}\text{H}_{80}\text{O}_{20}$ , the cold  $\text{C}_5\text{H}_{11}\cdot\text{OH}$ -sol. saponin from the  $\text{EtOH}$  extract of san-chi (0.26% of the drug), has m.p. 200—204° (decomp.),  $[\alpha]_{D}^{20} + 90.35^\circ$  in  $\text{H}_2\text{O}$  (deca-acetate, m.p. 255°), reduces Tollens' reagent but contains no  $\text{OMe}$  or phenolic group, and is hydrolysed (4%  $\text{EtOH}$ - $\text{HCl}$ ) to glucose and a sapogenin,  $\text{C}_{18}\text{H}_{28}\text{O}_{14}$ , m.p. 187—189°. A. Li.

**Position of the branching of the starch chain.** K. Freudenberg and H. Boppel (*Ber.*, 1940, **73**, [B], 609—620; cf. A., 1942, II, 6).—Hydrolysis of completely methylated starch (A., 1938, II, 51) by 36%  $\text{HCl}$  at 5° for 4 days gives (mainly) 2:3:6-trimethylglucose (I) (extracted with  $\text{CHCl}_3$ ), and a mother-liquor, converted by 1%  $\text{HCl}$ - $\text{MeOH}$ , followed by  $\text{Ag}_2\text{CO}_3$ , into a mixture of glucosides which yields a tri-, b.p. 100—110°/0.1 mm., and a di-methyl-methylglucoside, b.p. 110—125°/0.1 mm. After separating (I),  $\text{COMe}_2$  extracts of the hydrolysis mixture give (after glucosidation) tri- and di-methyl-methylglucoside. Fractions are treated with  $\text{BzCl}$ - $\text{C}_5\text{H}_5\text{N}$  at 80° and hydrolysed with  $\text{KOH}$ - $\text{MeOH}$  to give dimethyl-methylglucosides A and B, both of b.p. 120—125°/0.1 mm.; a tetramethyl-methylglucoside, b.p. 85°/0.1 mm., is isolated. 2:3-Dimethyl- $\alpha$ -methylglucoside and 2N-HCl at 100° (bath) for 6 hr., followed by azobenzene-*p*-carboxyl chloride in  $\text{C}_5\text{H}_5\text{N}$  at 40°, give 2:3-dimethylglucose tri-*p*-benzeneazobenzoate (C), m.p. 207°,  $[\alpha]_{D}^{20} + 97.8^\circ$  in  $\text{CHCl}_3$ , and an isomeride (D), m.p. 185° (sinters at 180°),  $[\alpha]_{D}^{20} + 35.4^\circ$  in  $\text{CHCl}_3$ . A affords a dimethylglucose tri-*p*-benzeneazobenzoate, m.p. 195—197°,  $[\alpha]_{D}^{20} + 49^\circ$  in  $\text{CHCl}_3$ , probably a mixture of C and D, whereas B yields C,  $[\alpha]_{D}^{20} + 92.5^\circ$  in  $\text{CHCl}_3$ , and an isomeride, m.p. 184° (sinters from 181°),  $[\alpha]_{D}^{20} + 57.7^\circ$  in  $\text{CHCl}_3$ . Although (I) is the main product of hydrolysis, methylated starch also affords a little 2:6- and 2:3-dimethyl-, and 2:3:4:6-tetramethyl-glucose; branching of the starch chain occurs at  $\text{OH}_{(6)}$ . Theoretical aspects are discussed, and photographs of models shown. A. T. P.

**Application of the end-group method to determining the composition of cellulose preparations.** K. Hess, D. Grigorescu, E. Steurer, and H. Frahm (*Ber.*, 1940, **73**, [B], 505—520).—Since natural, chemically untreated cellulose (I) does not afford tetramethylglucose, the end-group method can be used in determining the degradation caused by various technical processes. It is improved by the use of  $\text{MeOH}$  instead of  $\text{H}_2\text{O}$  for diluting the phosphorylation product which has been decomposed by  $\text{H}_2\text{O}$  and by avoiding diminished pressure in the distillation of light petroleum and  $\text{Et}_2\text{O}$  solutions, a suitable column being used. The products used have been subjected to the following pretreatments: (a) mild but thorough alkali boil in absence of air, (b) methylation in presence

of alkali and air, (c) technical processing in the case of ramie, (d) pptn. of (I) from alkaline solution, (e) pptn. from 65%  $\text{H}_2\text{SO}_4$ , (f) action of heat on solutions of methylcellulose in dioxan in presence and absence of air. Even with the best possible exclusion of air treatments (a) and (b) cause doubling of the end group, which is still more influenced by treatment (f). All the technical processes lead to end groups. It is doubtful whether it is justifiable to use the % end group of pretreated celluloses as a means of determining the mean chain length. H. W.

**End-group determination of polysaccharides.** K. Hess and D. Grigorescu (*Ber.*, 1940, **73**, [B], 499—505).—The examination of synthetic mixtures of tri- and tetra-methylmethylglucoside is not regarded as satisfactory for the criticism of Haworth's end-group method. The accuracy of the authors' own method is maintained. H. W.

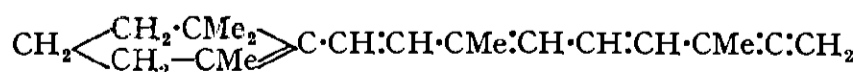
**Comparison of end-group determinations and viscosity of cellulose.** K. Hess and E. Steurer (*Ber.*, 1940, **73**, [B], 669—676).—Discrepancies between the degree of polymerisation of cellulose as determined by end-group (see above) and viscosity (generally gives lower vals.) methods are explained qualitatively by assuming 1 : 5 O bridges between glucose units of neighbouring cellulose chains. Fission of this linking and the normal glucosidic linking determines the effect of degradation on viscosity and end group content. Other evidence (lit.) is adduced in support of the assumption. A comparison of osmotic pressure, viscosity, and end-group content is made on three samples of methylcellulose. J. H. BA.

**Carbamates of cellulose and cellulose acetate. I. Preparation. II. Stability towards hydrolysis.** W. M. Hearon, G. D. Hiatt, and C. R. Fordyce (*J. Amer. Chem. Soc.*, 1943, **65**, 829—833, 833—836).—I. Partly hydrolysed cellulose acetate (I) scarcely reacts with HNCO and incompletely with MeNCO or EtNCO. Adding an excess of  $\text{PhNCO} \cdot \text{C}_6\text{H}_5\text{N}$  to (I) in dry  $\text{HCO} \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_5\text{N}$  or  $\alpha\text{-C}_{10}\text{H}_7 \cdot \text{NCO}$  (II) (excess) to (I) in dry  $\text{C}_6\text{H}_5\text{N}$  gives completely esterified products, sol. in cellulose ester solvents. Use of a deficiency of ArNCO leads to total consumption thereof and gives products containing residual OH and having reduced solubility. Reaction conditions are studied. At 4—50° 10 hr. suffices for complete reaction. HNCO, MeNCO, and EtNCO do not react with cotton linters or regenerated cellulose, but "low-viscosity" cotton linters with PhNCO or (II) in  $\text{C}_6\text{H}_5\text{N}$  at 100° (not 50°) gives sol. trisubstituted derivatives; <3 mols. of PhNCO give insol., fibrous products (III). ArNCO does not react in  $\text{C}_6\text{H}_5\text{N}$  at 100° or in quinoline at 150° with cellulose regenerated from the acetate, viscose, or cuprammonium rayon. Presence of  $\text{H}_2\text{O}$  in the reaction mixtures leads to  $\text{CO}(\text{NHAr})_2$ , and pptn. of the very insol.  $\text{CO}(\text{C}_{10}\text{H}_7\text{-a})_2$  by (II) in presence of a little  $\text{C}_6\text{H}_5\text{N}$  is a sensitive test for  $\text{H}_2\text{O}$  in solvents.

II. Acid hydrolysis of cellulose acetate arylcarbamates, e.g., by  $\text{H}_2\text{SO}_4$  in  $\text{OMe}[\text{CH}_2]_2\text{OH}$ , removes Ac at a const. rate, but does not affect the  $\text{NHAr} \cdot \text{CO}_2$  groups; drastic conditions, e.g., 100°, remove all the Ac but degrade the product. In suspension in aq. EtOH, alkali removes Ac rapidly and  $\text{NHAr} \cdot \text{CO}_2$  slowly; the resulting cellulose arylcarbamates are sol. in the usual solvents, in contrast to (III). R. S. C.

### III.—HOMOCYCLIC.

**Anhydro- ("cyclised") vitamin-A.** E. M. Shantz, J. D. Cawley, and N. D. Embree (*J. Amer. Chem. Soc.*, 1943, **65**, 901—906).—When vitamin-A (I) is treated in dil. solution with 0.033N-HCl-EtOH (cf. Edisbury *et al.*, A., 1932, 1174) (conc. solutions give mixed polymerides) and the product is purified by adsorption, it rapidly yields anhydrovitamin-A (II), m.p. 76—77°, having absorption max. at 351, 371, and 392  $\text{m}\mu$ . ( $E_{1\%}^{1\text{cm}}$ , 2500, 3650, and 3180, respectively) and giving with  $\text{SbCl}_3$  a max. at 620  $\text{m}\mu$ . ( $E_{1\%}^{1\text{cm}}$ , 5500); longer interaction gives isoanhydrovitamin-A, having absorption max. at ~330, 350, and 370  $\text{m}\mu$ . Probably, (II) is  $\text{C}_{20}\text{H}_{28}$ , having 6 C:C and no active H; it is unstable even at -35°/vac., more volatile than is (I) during short-path distillation, and is only weakly adsorbed. Distillation (short-path) partly decomposes the vitamin esters into (II). Three structures are suggested, the annexed being favoured. Formation of (II) is useful for determining mixtures of



vitamin- $A_1$  and - $A_2$  [anhydro- $A_2$  being more strongly adsorbed than is (II)] and for determining vitamin-A when other substances interfere, e.g., in blood plasma. R. S. C.

**Carotenoid pigments of fruit of *Celastrus scandens*.**—See A., 1943, III, 540.

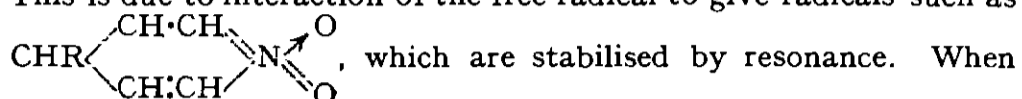
**Thermodynamics and molecular structure of benzene and its methyl derivatives.**—See A., 1943, I, 218, 223.

**Kinetics of aromatic hydrogenation. I. Bromination. II. Chlorination of hydrocarbons.**—See A., 1943, I, 231.

**Electrolytic reduction of arylacetylenes.**—See A., 1943, II, 249.

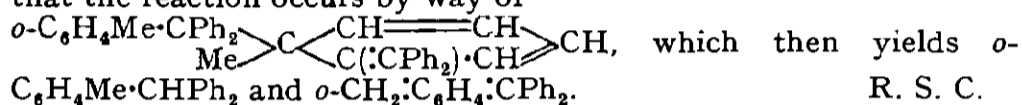
**Formation of biradicals in the non-catalysed polymerisation of styrene.** G. Goldfinger, H. Naidus, and H. Mark (*J. Amer. Chem. Soc.*, 1943, **65**, 995—996).— $\text{CHPh} : \text{CH}_2$  reacts with quinol at 150° giving PhMe and  $p\text{-O} : \text{C}_6\text{H}_4 : \text{O}$  (not isolated), probably by activation to give  $\cdot\text{CHPh} \cdot \text{CH}_2 \cdot$ . R. S. C.

**Polymerisation of styrene in presence of nitrobenzene, 2 : 4-dinitrochlorobenzene, and nitromethane.** C. C. Price and (Miss) D. A. Durham (*J. Amer. Chem. Soc.*, 1943, **65**, 757—759).— $\text{CHPh} : \text{CH}_2$  with  $\text{Bz}_2\text{O}_2$  and 1 : 2 : 4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$  (I) at 95—86° gives polymers,  $\text{OBz} \cdot (\text{C}_6\text{H}_5)_{10} \text{O}_2 \cdot \text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_2$ ,  $\text{OBz} \cdot (\text{C}_6\text{H}_5)_8 \text{O} \cdot \text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_2$ , and  $\text{OBz} \cdot (\text{C}_6\text{H}_5)_7 \text{O} \cdot \text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_2$ , but use of less (I) leads to a polymer containing <1 residue thereof per mol. Polymerisation in presence of  $\text{Bz}_2\text{O}_2$  and  $\text{PhNO}_2$  leads similarly to inclusion of both in the mol. This is due to interaction of the free radical to give radicals such as



this resonance is impossible, e.g., in  $\text{MeNO}_2$ , the  $\text{NO}_2$ -compound is not included in the polymer.  $\text{MeNO}_2$  also does not react at 100° with  $\text{Bz}_2\text{O}_2$ , which therein yields only  $\text{BzOH}$  and  $\text{Ph}_2$ . R. S. C.

**Disproportionation of diphenyl-*o*-tolylmethyl.** P. W. Selwood and R. F. Preckel (*J. Amer. Chem. Soc.*, 1943, **65**, 895—899).—Disproportionation of  $(o\text{-C}_6\text{H}_4\text{Me} \cdot \text{CPh}_2)_2$  at 80° and 95° is shown by magnetic measurements to be a second-order reaction having an activation energy 11.4 kg.-cal. per mol. of free radical. During the reaction absorption bands between 4200 and 5300 Å. disappear but those in the orange and red are unaffected; the absorption also becomes independent of temp. The mol. wt. (ebullioscopic) in  $\text{C}_6\text{H}_6$  appears to double during disproportionation. It is suggested that the reaction occurs by way of



R. S. C.

**Sesquiterpenes. LVIII. 4 : 8-Dimethyl-6-isopropylazulene.** P. A. Plattner and H. Roniger (*Helv. Chim. Acta*, 1943, **26**, 905—912).—Et 4 : 8-dimethylazulene-6-carboxylate is converted by a considerable excess of  $\text{MgMeI}$  in  $\text{Et}_2\text{O}$  into 4 : 8-dimethyl-6-hydroxyisopropylazulene (I), m.p. 54° [additive compound, m.p. 170°, with 1 : 3 : 5- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ ; does not give a stable picrate], with (?) 6-acetyl-4 : 8-dimethylazulene, characterised as the semicarbazone, m.p. ~212°. (I) is converted by  $\text{HCO}_2\text{H}$  at 100° into 4 : 8-dimethyl-6-isopropenylazulene (II), m.p. 70—71° [additive compound, m.p. 132°, with 1 : 3 : 5- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ ]. Hydrogenation (Pd-C in EtOH) of (II) leads to 4 : 8-dimethyl-6-isopropylazulene (III), m.p. 39° [picrate, m.p. 145°; additive compound, m.p. 173—173.5°, with 1 : 3 : 5- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ ]. Spectroscopically (III) falls into line with the other alkylazulenes (A., 1942, II, 191). M.p. are corr. H. W.

**Condensation of amino-alcohols with benzene.** C. M. Suter and A. W. Ruddy (*J. Amer. Chem. Soc.*, 1943, **65**, 762—763).— $\text{OH} \cdot \text{CMe}_2 \cdot \text{CHR}' \cdot \text{NHR}$  with  $\text{C}_6\text{H}_6$  and  $\text{AlCl}_3$  (excess) at room temp. (exothermally) and then the b.p. give  $\text{CPhMe}_2 \cdot \text{CH}_2 \cdot \text{NHR}$  [ $\text{R} = \text{H}$ , b.p. 87—89°/10 mm., Me, b.p. 92—92.5°/11 mm., or Et, b.p. 96—98°/11 mm. (hydrochloride, m.p. 191.5—192.5°)],  $\text{CPhMe}_2 \cdot \text{CHMe} \cdot \text{NHR}$  [ $\text{R} = \text{H}$ , b.p. 100—102°/10 mm. (hydrochloride, m.p. 214—215°), and Me, b.p. 99—100.5°/9 mm. (hydrochloride, m.p. 230—231°)], and  $\text{CPhMe}_2 \cdot \text{CMe}_2 \cdot \text{NH}_2$ , b.p. 123—126°/14 mm. (hydrochloride, m.p. 207—210°).  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OH}$  and  $\text{NH}_2 \cdot [\text{CH}_2]_2 \cdot \text{OH}$  do not react thus.  $\gamma$ -Methylamino- $\beta$ -methylbutan- $\beta$ -ol, b.p. 152—155°/750 mm., is obtained (85% yield) from trimethylethylene oxide and 33%  $\text{NH}_2\text{Me}$  at 100°. R. S. C.

**Sulphur studies. XIX. Alkyl esters of phenylthiocarbamic acid.** R. W. Bost and E. R. Andrews (*J. Amer. Chem. Soc.*, 1943, **65**, 900—901; cf. A., 1942, II, 284).— $\text{ArNCS}$  in boiling AlkOH gives 31—90% of  $\text{NHAr} \cdot \text{CS} \cdot \text{OR}$ . When AlkOH is readily dehydrated [e.g.,  $\text{CH}_2 : \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$ ,  $\text{Bu}^n\text{OH}$ ,  $(\text{CH}_2\text{OH})_2$ ,  $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{OH}$ , tetraethylhexanediol, pinacol], only  $\text{CS}(\text{NHPh})_2$  is thus obtained; the esters are then prepared from  $\text{AlkONa}$  and  $\text{ArNCS}$ .  $\text{Bu}^n$ , m.p. 51—53°,  $\text{Bu}^i$ , m.p. 86.5°,  $n$ -, m.p. 49—50°, and iso-amyl, m.p. 44—46°,  $n$ -heptyl, m.p. 34°,  $n$ -octyl, m.p. 41—43°,  $n$ -nonyl, m.p. 45—47°,  $\beta$ -phenylethyl, m.p. 89.5°,  $\gamma$ -phenyl- $n$ -propyl, m.p. 74°, and allyl  $N$ -phenylthiocarbamate, m.p. 75—77°, are described. 20 thiocarbamates are non-hypnotic, possibly because of their insolubility in  $\text{H}_2\text{O}$ . R. S. C.

***N*-Nitrosoacet-1-naphthalide.** H. H. Hodgson and E. Marsden (*J.C.S.*, 1943, 285).—*N*-Nitrosoacet-1-naphthalide, m.p. 8—10°, is formed when  $\alpha\text{-C}_{10}\text{H}_7 \cdot \text{NHAc}$  in AcOH is added to  $\text{NO} \cdot \text{SO}_3\text{H}$ . Its reactions are similar to those of a diazonium compound in mineral acid (e.g., Sandmeyer) and a diazo-compound in neutral, weak acid, and alkaline solution. F. R. S.

**Identification of carboxylic acids as ureides with the help of carbodi-imides. VIII. Ureides of symm. di-*p*-diethylaminophenylcarbamide.** F. Zetzsche and G. Röttger. IX. Preparation of carbodi-imides from thiocarbamides. F. Zetzsche and W. Neger [with, in part, G. Röttger and A. Friedrich] (*Ber.*, 1940, **73**, [B], 465—467, 467—477).—VIII. Replacement of Me of *N*-acyl- $\text{NN}'$ -di-

*p*-dimethylaminophenylcarbamides by Et causes a not very pronounced darkening of colour, a lowering of the m.p., and a very marked increase in solubility.  $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  and the imide in  $\text{Et}_2\text{O}$  afford *N*-crotonyl-*NN'*-di-*p*-diethylaminophenylcarbamide, m.p. 130—132°. The corresponding ureides of cinnamic, m.p. 83°, tiglic, m.p. 106—108°, atropic, m.p. 124.5—126.5°, benzoic, m.p. 121.5° (softens at 119°), and  $\beta$ -pyrenoylpropionic (I), m.p. 159°, and the diureide, m.p. 151° and 210° after resolidifying at 152°, of fumaric acid are obtained analogously. The methylureide of (I) has m.p. 162—163° (softens at 159°) (cf. A., 1939, II, 467).

IX. In comparison with ordinary  $\text{PbO}$ , the highly disperse material ("tegoglätte") accelerates the desulphurisation of arylthiocarbamides (II) to carbodiarylimides (III). Increase in the reacting surface also favours the subsequent conversion of (III) into carbamides or resinous products. These primary and secondary reactions are also accelerated by  $\text{H}_2\text{O}$ . S accelerates the primary reactions and also decelerates the secondary changes; it largely counteracts the effect of  $\text{H}_2\text{O}$ . As long as (II) is present in the system it fulfils the rôle of S towards the subsidiary reactions. A solvent miscible with  $\text{H}_2\text{O}$  is very desirable but only  $\text{COMe}_2$  appears completely suitable;  $\text{COMeEt}$  is generally similar but the higher b.p. diminishes the restricting action of S on the production of carbamides. "Tegomennige" is serviceable. Se appears to resemble S in its action. The course of the change depends greatly on the purity of (II) and the prep. of standard  $\text{CS}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot p)_2$  is fully described. The prep. of small and large amounts of  $\text{C}(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Me}\cdot p)_2$  and  $\text{C}(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot p)_2$  is detailed. Carbodi-*p*-diethylaminophenylimide has m.p. 81—82°, softens at 79°. *N'*-Benzene-azo-*N*-phenylcarbodi-imide, m.p. 60—64°, gives the corresponding benzoylureide, m.p. 117—118° and 156—157° after resolidification at 122°, and cinnamureide, m.p. 117—118° and 140° after partial resolidification at 130°. H. W.

**Partial hydrolysis of *N'**N'*-diacetylsulphanilamide. Preparation of *N'*-acetylsulphanilamide.** H. Minlon and C. P. Lo (*J. Chinese Chem. Soc.*, 1942, 9, 61—65).— $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$  and  $\text{Ac}_2\text{O}$ — $\text{AcOH}$  give  $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHAc}$ , m.p. 258—259°, hydrolysed by boiling 10%  $\text{KOH}$ — $\text{EtOH}$  to  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHAc}$ , m.p. 181—182°.  $(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHAc}\cdot p)_2$  is similarly unchanged, but is hydrolysed by boiling 10% aq.  $\text{KOH}$  to the diamide. A. T. P.

***N'*-( $\beta$ -Acylamino- $\beta$ -carboxyethylthiomethyl)sulphanil-hydroxyl-amides and  $\beta$ -hydroxyethylamides.**—See B., 1943, III, 193.

**Sulphanilylalkylguanidines.**—See B., 1943, II, 243.

**Identification of sulphonic acid reduction products of azo-dyes.** P. Chen and E. J. Cross (*J. Soc. Dyers & Col.*, 1943, 59, 144—148).—Monosulphonic acids of  $\text{NH}_2\text{Ph}$ ,  $\alpha$ - and  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ , 1:2- and 1:4- $\text{C}_{10}\text{H}_8(\text{NH}_2)_2$ , and  $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$  are identified as the  $\text{C}_6\text{H}_5\text{N}$  salts of their Ac derivatives; the salts are stable, can be cryst. from  $\text{EtOH}$ , and have sharp m.p. *E.g.*, the dry, finely-powdered sulphonic acid (2 g.) is stirred with  $\text{C}_6\text{H}_5\text{N}$  (1.2) and  $\text{Ac}_2\text{O}$  (2.5 c.c.), whereupon exothermic dissolution occurs; the solution is then diluted with  $\text{EtOH}$ , the solid is collected, washed with  $\text{EtOH}$ , and recryst. The salts are very sol. in  $\text{H}_2\text{O}$ , some being hygroscopic, and they are convertible by double decomp. into known arylamine salts, *e.g.*, by adding *p*-toluidine to the hot aq. solution. In some cases where  $\text{C}_6\text{H}_5\text{N}$  salts could not be made the sulphonic acid was heated with  $\text{C}_6\text{H}_5\text{N}$  and  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ , giving  $\text{C}_6\text{H}_5\text{N}$  phthalanil-sulphonates. The following are described:  $\text{C}_6\text{H}_5\text{N}$  phthalanil-2', m.p. 236—237°, -3', m.p. 219—220°, and -4'-sulphonate, m.p. 225—226°;  $\text{C}_6\text{H}_5\text{N}$  acetanilid-4-sulphonate, m.p. 183—184°; *p*-toluidinium 1-acetamidonaphthalene-2-, m.p. 205—206°, 2-acetamidonaphthalene-1-, m.p. 178—179°, -5-, m.p. 118—119°, and -7-sulphonate, m.p. >300° (softens 260°);  $\text{C}_6\text{H}_5\text{N}$  1-acetamidonaphthalene-4-, m.p. 175—176°, -5-, m.p. 194—195°, -6-, m.p. 157—158°, -7-, m.p. 196—197°, 2-acetamidonaphthalene-6-, m.p. 171—172°, and -8-sulphonate, m.p. 183—184°;  $\text{C}_6\text{H}_5\text{N}$  2-phthalimidonaphthalene-5-sulphonate, m.p. 255—256° (softens 245°);  $\text{C}_6\text{H}_5\text{N}$  1:2-diacetamidonaphthalene-4-, m.p. 223—224°, -5-, m.p. >300°, -6-, m.p. 229—230°, and 1:4-diacetamidonaphthalene-6-sulphonate, m.p. 247—248° (decomp.); *p*-toluidinium 1:2-diacetamidonaphthalene-4-, m.p. 213—214° (decomp.) (softens 195°), -5-, m.p. 188—189° (decomp.) (softens 174°), and -6-sulphonate, m.p. 249—250° (decomp.);  $\text{C}_6\text{H}_5\text{N}$  ON-diacetyl-1:2:4-, m.p. 194—195°, -1:8:4-, m.p. 203—204° (decomp.), -2:1:4-, m.p. 181—182°, and -2:1:5-aminonaphtholsulphonate, m.p. 196—197°;  $\text{C}_6\text{H}_5\text{N}$  2:8:6-, m.p. 245—246°, and 2:5:7-acetamidonaphtholsulphonate, m.p. 190—191°; *p*-toluidinium ON-diacetyl-1:2:4-, m.p. 213—214° (decomp.), -1:2:6-, m.p. 209—210°, and -2:8:6-aminonaphtholsulphonate, m.p. 230—231°, and 2-acetamido-8-naphthol-6-sulphonate, m.p. 282—283°. K. H. S.

**Behaviour of azobenzene and hydrazobenzene towards methyl iodide; the benzidine transformation.** A. Pongratz and H. Wüstner (*Ber.*, 1940, 73, [B], 423—429).— $(\text{NPh})_2$  is converted by MeI at 100° into tetramethylbenzidine dimethiodide tetraiodide (I), incipient carbonisation at 320°, transformed by aq.  $\text{NaHSO}_3$  into tetramethylbenzidine dimethiodide (+1— $2\text{H}_2\text{O}$ ), m.p. 250—252° to 262—266°, which with  $\text{KOH}$ — $\text{EtOH}$  yields  $(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , new m.p. 190—191.7°. (I) is also obtained from  $(\text{NHPh})_2$  and MeI or  $\text{MeOH}$ —MeI at 100°

whereas  $(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$  and MeI in absence of  $\text{MeOH}$  afford  $(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , MeI (II). The isomerisation of  $(\text{NPh})_2$  or  $(\text{NHPh})_2$  to derivatives of  $(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$  (by MeI) shows that Me does not become attached to N by subsequent methylation but is added to the N:N or NH:NH bridge previous to isomerisation with formation of salt-like compounds. The production of (II) but not (I) from  $(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$  shows the distinction between methylation of pre-formed  $\text{NH}_2$  groups and the "primary methylation." The formation of an additional intermediate is supported by Wieland's isolation of  $(\text{NHPh})_2\cdot 2\text{HCl}$ . H. W.

**Substituted azobenzene-4:4'-disulphonamides.** H. Minlon, C. P. Lo, and L. J. Y. Chu (*J. Chinese Chem. Soc.*, 1942, 9, 57—60).— $(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}\cdot p)_2$  and the respective amine yield azobenzene-4:4'-disulphonamide, m.p. 312° (*s*- $\text{Ac}_2$  derivative, m.p. 273°), -diethyl-, m.p. 171—172°, -dipropyl-, m.p. 140—150°, -benzyl-, m.p. 252—253°, and -2-pyridyl-amide, m.p. 274—276°, -anilide, m.p. 255—256°, and -anilide-*p*-sulphonamide, m.p. 310°. A. T. P.

**Azo-compounds and their intermediates. XXIV. Hydrazo-compounds of di(benzeneazo)diphenyl.** P. Ruggli and K. Hölzle (*Helv. Chim. Acta*, 1943, 26, 814—832; cf. A., 1943, II, 158).—4:4'-Di-(benzeneazo)diphenyl (I) [prep. from benzidine (II) and  $\text{PhNO}$  described] absorbs 4 H (Raney Ni in  $\text{EtOH}$  or dioxan) whereby one half remains unchanged and the other half is converted into  $\text{NH}_2\text{Ph}$  and (II). The result is ascribed to the sparing solubility of (I). Addition of  $\text{AcOH}$  to (I) in  $\text{C}_6\text{H}_5\text{N}$  containing Zn dust under  $\text{CO}_2$  affords 4:4'-di-(phenylhydrazino)diphenyl (III), m.p. 177—178° (slight decomp.) after becoming yellow, which becomes superficially yellow within a few min. in air but can be preserved for some days in a high vac. In  $\text{C}_6\text{H}_5\text{N}$  it is rapidly converted by air into (I). Under different conditions (III) suffers intramol. disproportionation into *p*- $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot p$  and  $\text{NH}_2\text{Ph}$  or extramol. disproportionation to (I), (II), and  $\text{NH}_2\text{Ph}$ . In  $\text{C}_6\text{H}_5\text{N}$  under  $\text{CO}_2$  2*N*-HCl causes 88% of intramol. and 4% of extramol. disproportionation whereas with a small excess of  $\text{AcOH}$  the figures are 65% and 15%.  $\text{AcSH}$  causes 58% intramol. disproportionation with acetylation of the fragments. The  $\text{Ac}_2$  derivative, m.p. 235° (carbonisation), of (III) is obtained in poor yield by protracted action of a little  $\text{Ac}_2\text{O}$  in cold  $\text{COMe}_2\text{-C}_6\text{H}_5\text{N}$ ; reductive fission slowly yields  $(\text{C}_6\text{H}_4\cdot\text{NHAc}\cdot p)_2$  and  $\text{NH}_2\text{Ph}$ . Cautious treatment of (III) with conc.  $\text{H}_2\text{SO}_4$  causes much decomp.; acetylation of the product gives only  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ . (III), Sn, and HCl afford only (II) and  $\text{NH}_2\text{Ph}$  (mol. ratio 1:2). Above its m.p. (III) passes into (I), (II), and  $\text{NH}_2\text{Ph}$ . 4-Amino-4'-benzeneazodiphenyl (IV), m.p. 151—152°, obtained in the above disproportionations, is prepared by the condensation of (II) with  $\text{PhNO}$  (1 mol.) or by reduction of 4-nitro-4'-benzeneazodiphenyl (V) with  $\text{Na}_2\text{S}$  in boiling  $\text{EtOH}$ —dioxan; the  $\text{CHPh}$ , m.p. 226°, *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}$ , m.p. 214—215°, and *Ac* derivative, m.p. 236—237°, of (IV) are described. Contrary to Vorländer *et al.* (A., 1925, i, 1253), reduction of (V) by  $(\text{NH}_4)_2\text{S}$  gives 4-nitro-4'-phenylhydrazinodiphenyl, m.p. 164—165° (*Ac* derivative, m.p. 161°), converted by air into (V). Under defined conditions (I) is reduced by Zn dust and  $\text{AcOH}$  in  $\text{C}_6\text{H}_5\text{N}$  to 4-phenylhydrazino-4'-benzeneazodiphenyl (VI), m.p. 172—173°, converted by  $\text{Ac}_2\text{O}$  in boiling  $\text{C}_6\text{H}_5\text{N}$  into *Ac* derivatives (VII)  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NAc}\cdot\text{NHPh}$ , m.p. 244°, and (VIII)  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NPhAc}$ , m.p. 194—195°. (VII) is hydrogenated in dioxan to  $\text{NH}_2\text{Ph}$  and 4-amino-4'-*a*-acetyl- $\beta$ -phenylhydrazinodiphenyl, m.p. 220°, which is further hydrogenated to  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , whereas (VIII) affords  $\text{NH}_2\text{Ph}$ , (II), and  $\text{NHPhAc}$ . (VI) is converted by HCl in  $\text{COMe}_2$  at 20—30° into  $\text{NH}_2\text{Ph}$ , (I), and (IV). (III) and  $(\text{C}\cdot\text{CO}_2\text{Me})_2$  give an adduct, m.p. 124—125°. H. W.

**Manufacture of thymol.**—See B., 1943, II, 244.

**Bromination of 4-diphenyl bromoacetate.** L. C. Hensley and S. E. Hazlet (*J. Amer. Chem. Soc.*, 1943, 65, 987—988; cf. A., 1943, II, 59).—3-Bromo-, m.p. 55—56°, 3:5-dibromo-, m.p. 78—79°, 3:5:4'-tribromo-, m.p. 148—149°, and 4'-bromo- (I), m.p. 141.5—142°, 4-diphenyl bromoacetate are prepared from the phenol,  $\text{CH}_2\text{Br}\cdot\text{COBr}$ , and  $\text{C}_6\text{H}_5\text{N}$  in dioxan.  $\text{CH}_2\text{Br}\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\text{Ph}\cdot p$ , Br, and a trace of Fe powder in  $\text{AcOH}$  (analytical grade) give *p*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{OAc}$  and a little *p*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{OH}$  (II), 4:2:6:1- $\text{C}_6\text{H}_2\text{PhBr}_2\cdot\text{OH}$ , and 1:2:6:4- $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{C}_6\text{H}_4\text{Br}\cdot p$ , but in highly purified  $\text{AcOH}$  no bromination occurs [a little (II) is formed]; in  $\text{CCl}_4$ , (I) is obtained. R. S. C.

**Peroxide degradation of substituted aromatic aldehydes and ketones to the corresponding phenol.** A. von Wacek and H. O. Eppinger (*Ber.*, 1940, 73, [B], 644—651).—Although *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  (I) and 30%  $\text{H}_2\text{O}_2$  at 60—80°, alone or in  $\text{COMe}_2$  (in absence or presence of Pd), yield 60—70% of *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  (II) and only traces of *o*- $\text{C}_6\text{H}_4(\text{OH})_2$  (III), in boiling  $\text{AcOH}$  90% of (III), a little resin, and no (II) result. In boiling  $\text{C}_6\text{H}_5\text{N}$ , 75% of (II) and 25% of (III) are formed, but only traces of (III) from (I)— $\text{H}_2\text{O}_2$ — $\text{COMe}_2$  at 120° in a sealed tube. *o*- (IV), *m*- (V), or *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  (VI) and aq.  $\text{H}_2\text{O}_2$ — $\text{NaOH}$  give negative reactions, as also does (V) and  $\text{O}_3$ . (IV) and  $\text{O}_3$ — $\text{CHCl}_3$ , however, yield ~3% of *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  and (mainly) *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ ; (VI) and *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$  similarly give 4—5% of *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ . 7-Hydroxy-1-hydrindone is similarly

unchanged. A probable reaction mechanism is, e.g., (I)  $\rightarrow$   $o$ -CHO·C<sub>6</sub>H<sub>4</sub>·O·OH  $\rightarrow$   $o$ -OH·C<sub>6</sub>H<sub>4</sub>·O·CHO  $\rightarrow$  (III).  
A. T. P.

**Introduction of allyl residues into aromatic compounds.** P. Karrer and E. Schick (*Helv. Chim. Acta*, 1943, 26, 800—807).—Among Me-substituted derivatives of dihydric phenols those of quinol occupy a favoured position with regard to reactivity towards allyl halides. The corresponding C-Me derivatives of  $o$ - and  $m$ -C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> react with allyl halides and ZnCl<sub>2</sub> as catalyst only slightly if at all to give coumaran or chroman derivatives. 2:4:6:1-(OH)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Me·CH·NPh is reduced (H<sub>2</sub> at 117—120°/20 atm.—Pd—C—COMe<sub>2</sub>) to 4:5-dimethylresorcinol (I), m.p. 134—135°. 2:4:5:6:1-(OH)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·CHO, m.p. 196° [prep. from 4:5:1:3-C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>(OH)<sub>2</sub> described], is converted into the anil, m.p. 188°, which is reduced to 4:5:6:1:3-C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>(OH)<sub>2</sub> (II), m.p. 163°. (I) gives no definite product with CH<sub>2</sub>:CH·CH<sub>2</sub>Br and ZnCl<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> whilst (II) gives traces of a compound, m.p. 120—121°, possibly a hydroxytetramethylcoumaran. Veratraldehydeanil is hydrogenated to homo-veratrole, converted (HCN—AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub>) into 6-methylveratraldehyde; this gives an anil, m.p. 92.5—93.5°, hydrogenated to 4:5-dimethylveratrole, b.p. 120—121°/13 mm., m.p. 43—43.5°, into which CHO could not be introduced by HCN—AlCl<sub>3</sub>—HCl. 4:5:1:2-C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>(OH)<sub>2</sub> appears to be converted by CH<sub>2</sub>:CH·CH<sub>2</sub>Br and anhyd. ZnCl<sub>2</sub> in warm C<sub>6</sub>H<sub>6</sub> into 6-hydroxy-1:3:4-trimethyl-5-allylcoumaran, isolated as the *allophanate*, m.p. ~166—169°. 4:5-Dimethylguaiacol has m.p. 67—68°. H. W.

**4:4'-Dihydroxy-3:3'-dicyclohexyldiphenyl.**—See B., 1943, II, 244.

**Reaction of phenols with acetylene.** H. von Euler, E. Adler, and J. O. Cedwall (*Arkiv Kemi, Min., Geol.*, 1942, 15, A, No. 19, 10 pp.).— $m$ -4-Xylenol (I) and C<sub>2</sub>H<sub>2</sub> in MeOH—HgSO<sub>4</sub>—conc. H<sub>2</sub>SO<sub>4</sub> (less well in EtOH) at 60—70° give *aa*-di-(2-hydroxy-3:5-dimethylphenyl)ethane (II) (~100%), m.p. 135—135.5° (*diacetate*, m.p. 93—94°) [also obtained from (I) and MeCHO in EtOH—conc. HCl]. Addition of (I) (as above but in EtOH at 70—80°) with C<sub>2</sub>H<sub>2</sub> always in excess, gave a fraction, b.p. 100—105°/12 mm., in which the expected intermediate 1:2:4:6-OH·C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·CH:CH<sub>2</sub> was detected but could not be isolated. (I) and C<sub>2</sub>H<sub>2</sub> in AcOH—HgSO<sub>4</sub> at 60—70° give (II) and the cyclic CHMe: ether (III), m.p. 185.5—186.5°, of (II). (III) with dry HBr in CHCl<sub>3</sub> at room temp. gives (II). (III) is also obtained from C<sub>2</sub>H<sub>2</sub> and (II) in AcOH—HgSO<sub>4</sub> at 90°, and from (II) and CHMeCl<sub>2</sub> with KOH—50% EtOH (1 hr. at 120° in sealed tube; 2% yield). M. H. M. A.

**$\gamma$ -Alkylamino- and  $\gamma$ -alkoxy- $\alpha$ -aryloxypropan- $\beta$ -ols and - $\beta$ -ones.**—See B., 1943, II, 244.

**Synthesis of methoxy-methylenedioxydiphenyls and a new fluorenone cyclisation.** S. Uyeo (*Ber.*, 1940, 73, [B], 661—669).—5-Bromopiperonal (I),  $o$ -C<sub>6</sub>H<sub>4</sub>I·OMe, and Cu at 220—230° give (2-OMe·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> and 2-methoxy-2':3'-methylenedioxydiphenyl-5'-aldehyde, b.p. 185—190°/1.5 mm.; the latter with KMnO<sub>4</sub>—COMe<sub>2</sub> at 50° gives the corresponding 5'-carboxylic acid, m.p. 233°, converted by quinoline—Cu chromite (Adkins) into 2-methoxy-2':3'-methylenedioxydiphenyl, m.p. 103.5—104°. (I) and  $p$ -C<sub>6</sub>H<sub>4</sub>I·OMe afford 4-methoxy-2':3'-methylenedioxydiphenyl-5'-aldehyde, m.p. 143°, and 5'-carboxylic acid, m.p. 261—262°, and thence 4-methoxy-2':3'-methylenedioxydiphenyl, m.p. 128—129°. 6-Bromopiperonal and  $o$ - or  $p$ -C<sub>6</sub>H<sub>4</sub>I·OMe yield 2- (II), m.p. 142°, or 4-methoxy-3':4'-methylenedioxydiphenyl-6'-aldehyde (III), m.p. 105—106°, the corresponding acids, m.p. 201—202° resolidifying with m.p. 206—207°, or 225—226°, and thence 2-, m.p. 56—57°, or 4-methoxy-3':4'-methylenedioxydiphenyl, m.p. 97—98°, respectively. In preparing (II) and (III), chromatographic separation of the reaction products yields 4- (IV), m.p. 175—177° [*oxime*, m.p. 264° (decomp.)], and 2-methoxy-6:7-methylenedioxyfluorenone, m.p. 188° [*oxime*, m.p. 218—219° (decomp.)], respectively. (IV) is also obtained from (II) and Cu at 230—240°. A. T. P.

**$\beta\beta$ -Dimesitylvinyl alcohol.** R. C. Fuson and S. P. Rowland (*J. Amer. Chem. Soc.*, 1943, 65, 992—993).—Hydro- or isohydro-mesitoin with dehydrating agents gives  $\beta\beta$ -dimesitylvinyl alcohol (I) (60%), m.p. 128—129°, which with MgMeI gives 1 mol. of CH<sub>4</sub>, gives an acetate, benzoate, and Me ether which regenerate (I) on hydrolysis, has infra-red absorption max. at 2.77 and 2.84  $\mu$ . in CCl<sub>4</sub>, is stable to heat and O<sub>2</sub>, and with alkaline H<sub>2</sub>O<sub>2</sub> gives dimesityl ketone. R. S. C.

**Possible new member of the vitamin-A<sub>1</sub> and -A<sub>2</sub> group.** N. D. Embree and E. M. Shantz (*J. Amer. Chem. Soc.*, 1943, 65, 906—909).—The more volatile (short-path distillation) portion of the unsaponifiable fraction of shark-liver oil is extracted in 83% EtOH by light petroleum; the material from the EtOH is adsorbed from C<sub>6</sub>H<sub>6</sub> on Al<sub>2</sub>O<sub>3</sub> and developed by Et<sub>2</sub>O—light petroleum; the yellow zone immediately below the top (light-brown) one yields subvitamin-A (I), which has an absorption max. at 290 m $\mu$ , gives a SbCl<sub>3</sub> colour with a max. at 617 m $\mu$ , is relatively sol. in 83% EtOH, and has little or no -A activity. Dehydration of the original oil or of (I) leads to anhydrosbvitamin-A (II), which has absorption max. at 332, 348, and 367 m $\mu$  and is absorbed much more strongly than

is anhydrovitamin-A<sub>1</sub> and slightly more strongly than is anhydrovitamin-A<sub>2</sub>. Elimination temp. (short-path distillation) of (I), anhydrovitamin-A<sub>1</sub> and -A<sub>2</sub> are, respectively, 15° above, 19° and 1° below, and that of (II) is the same as, that of celanthrene-red dye (123°). (I) is probably an oxygenated derivative of vitamin-A<sub>1</sub> or -A<sub>2</sub> but has one less ethylenic linking. R. S. C.

**Kitol, a new provitamin-A.** N. D. Embree and E. M. Shantz (*J. Amer. Chem. Soc.*, 1943, 65, 910—913).—Kitol (I) is isolated from the less volatile "vitamin fractions" of whale-liver oil and in small amounts from commercial shark- and lamb-liver oil. It is probably C<sub>40</sub>H<sub>58</sub>(OH)<sub>2</sub>, contains 8 C:C, gives a *bisdinitrobenzoate*, m.p. 200°, has  $[\alpha]_{D}^{25} -1.35^\circ$  in CHCl<sub>3</sub>, gives no anhydro-derivative, has an absorption max. at 286 m $\mu$ . ( $E_{1\%}^{1\text{cm}}$  580) (SbCl<sub>3</sub> max. at 428 m $\mu$ ), has little or no biological activity, but when pyrolysed yields vitamin-A (1 mol. per mol.). It is thus a true provitamin. The liver oil of northern pike probably contains kitol<sub>2</sub>, a provitamin-A<sub>2</sub> (absorption max. at 310 m $\mu$ ; SbCl<sub>3</sub> max. at 510 m $\mu$ ). R. S. C.

**Photo-reactions. VI. Formation of benzpinacol by the action of acetone on benzhydrol in sunlight.** A. Schönberg and A. Mostafa (*J. C. S.*, 1943, 276).—The reaction 2CHPh<sub>2</sub>·OH + COMe<sub>2</sub> (or COMeEt)  $\rightarrow$  (CPh<sub>2</sub>·OH)<sub>2</sub> + Pr $\beta$ OH (or CHMeEt·OH) occurs in sunlight in absence of air. F. R. S.

**[ $\beta$ ]-Phenyl- and [ $\beta$ ]-benzyl-thiolpropionic acids and their oxidation products.** B. Holmberg and E. Schjånberg (*Arkiv Kemi, Min., Geol.*, 1942, 15, A, No. 20, 14 pp.; cf. A., 1943, II, 157).—PhSNa and I·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H, or PhSH (I) and CH<sub>2</sub>:CH·CO<sub>2</sub>H (II), give  $\beta$ -phenylthiolpropionic acid (III), m.p. 60—61°, decomposed by aq. NaOH at 100° to (I) and (II). (III) and CH<sub>2</sub>Br·CO<sub>2</sub>Na give SPh·CH<sub>2</sub>·CO<sub>2</sub>Na and (II), presumably via Ph·S<sup>+</sup>(CH<sub>2</sub>·CO<sub>2</sub>)<sup>-</sup>·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>Na which could not be isolated. (III) is oxidised (Na<sub>2</sub>O<sub>2</sub>) to  $\beta$ -phenylsulphinylpropionic acid (IV), m.p. 97—99°, which reacts with aq. NaOH at 100° thus: (IV)  $\rightarrow$  Ph·SOH (V) + (II); 3(V)  $\rightarrow$  PhSO<sub>2</sub>H (VI) + Ph<sub>2</sub>S<sub>2</sub> (isolated) + H<sub>2</sub>O; (VI) + (II)  $\rightarrow$  PhSO<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H (VII) (isolated). (VII), from (IV) with Br—NaOH or KMnO<sub>4</sub>, or from (VI) and (II), has m.p. 125.5—127° (cf. A., 1888, 360) (*mono*-, m.p. 58—60°, clear at ~90°, and *tri-hydrate*, m.p. 65—67°) (cf. A., 1908, i, 21). (VII) is stable to 2N-HCl (4 hr. at 100°), but with dil. NaOH gives (II) and (VI). CH<sub>2</sub>Ph·S·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H, like (III), forms a thetine which could not be isolated, and is oxidised (H<sub>2</sub>O<sub>2</sub> or K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) to  $\beta$ -benzylsulphinylpropionic acid, m.p. 149—150° (decomp.), which with NaOH aq. at 100° gives (S·CH<sub>2</sub>Ph)<sub>2</sub> and CH<sub>2</sub>Ph·SO<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H by reactions similar to those of (IV). M. H. M. A.

**Phenylethylthiolpropionic acids and related compounds.** B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1942, 15, A, No. 21, 16 pp.; cf. A., 1939, II, 158, 546; 1942, II, 157).—CHPhMe·OH and SH·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H (I) give (4 hr. at 100°) dl- $\beta$ - $\alpha'$ -phenylethylthiolpropionic acid (II), m.p. 58—59°. CH<sub>2</sub>Ph·CH<sub>2</sub>·SNa and I·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H with HCl (2 days at room temp.) or CHPh·CH<sub>2</sub> and (I) (3 days at room temp.) give  $\beta$ - $\beta'$ -phenylethylthiolpropionic acid (III), m.p. 46—47°. (II) and (III) are stable to hot dil. NaOH and hot dil. HCl, and (III) to HgCl, whilst with (II) the reaction of formation is reversed. (II), but not (III), shows evidence of thetine (not isolated) formation with CH<sub>2</sub>Br·CO<sub>2</sub>Na. With Br—AcOH (II) yields (S·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub> and CHPhMeBr, while (III) is oxidised to SO- and SO<sub>2</sub>-acids (below). (II) and (III) with H<sub>2</sub>O<sub>2</sub> or K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> give respectively  $\beta$ - $\alpha'$ - (IV), diastereoisomeric mixture, m.p. 79—81° (clear at 83—84°) (H<sub>2</sub>O<sub>2</sub>), m.p. 86—87° (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), and  $\beta$ - $\beta'$ -phenylethanesulphinyl- (V), m.p. 111—112°, and thence or directly from (II) and (III) [KMnO<sub>4</sub>; Br—H<sub>2</sub>O with (III) only] dl- $\beta$ - $\alpha'$ - (VI), m.p. 174—175°, and  $\beta$ - $\beta'$ -phenylethanesulphonyl-propionic acid (VII), m.p. 142—143°, respectively. (IV) [and similarly (V)] is hydrolysed (dil. alkali) to (S·CHPhMe)<sub>2</sub> and CH<sub>2</sub>:CH·CO<sub>2</sub>H (VIII); (VI) [via CHPhMe·SOH (not isolated)] (cf. preceding abstract) and (VII) give (VIII) and  $\alpha$ - (IX), m.p. 55—65° (+1H<sub>2</sub>O, m.p. 50—65°), and  $\beta$ -phenylethanesulphinic acid (X), m.p. 58—59°, respectively ( $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> salts, sinters at 95°, brown at 150°, no m.p., and m.p. 123—124° respectively). (IX), but not (X), oxidises rapidly in air. M. H. M. A.

**Oxidation of mercaptal- and mercaptol-acids with persulphate.** B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1942, 15, A, No. 24, 8 pp.).—Oxidation (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) of CR'R''(S·CH<sub>2</sub>·CO<sub>2</sub>Na)<sub>2</sub> [from SH·CH<sub>2</sub>·CO<sub>2</sub>H and COR'R'' (I)] gives usually CR'R''(SO·CH<sub>2</sub>·CO<sub>2</sub>Na)<sub>2</sub> (R', R'' = H, alkyl, aralkyl, CO<sub>2</sub>H, etc.), but when R' = H, R'' = 3:4-OMe·C<sub>6</sub>H<sub>3</sub>(OH), 3:4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (partly), (I) and (S·CH<sub>2</sub>·CO<sub>2</sub>Na)<sub>2</sub> are formed, and when R' = H, R'' = 3:4-CH<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>, CHPh·CH<sub>2</sub>·CO<sub>2</sub>Na, 3:4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (partly), or R' = Ph, R'' = H, Me, Ph, CR'R''<O·CO is formed, but could not always be isolated. The following are described:  $\alpha$ -hydroxy-3:4-dimethoxy-, m.p. 110—111.5°, and -3:4-methylenedioxy-benzyl-, m.p. 65—66°, and  $\alpha$ -hydroxycinnamyl-, m.p. 111—112°, -thiolacetic acid lactones. CHPh(S·CHMe·CO<sub>2</sub>Na)<sub>2</sub> gives similarly  $\alpha$ - $\alpha'$ -hydroxybenzylthiolpropionic acid lactone, diastereoisomerides, m.p. 65—73° (impure) and 77—78°, but CHPh(S·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>Na)<sub>2</sub> does not give a lactone. M. H. M. A.

**NN'-Substituted  $\alpha$ -aminodiphenylacetamides.** J. H. Billman and P. H. Hidy (*J. Amer. Chem. Soc.*, 1943, 65, 760—761).—CPh<sub>2</sub>Cl·COCl

(prep. from  $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$  and  $\text{PCl}_5$  improved to give 65–80% yield) and  $\text{NH}_2\text{R}$  in  $\text{Et}_2\text{O}$  give 5–57% of  $\text{NHR}\cdot\text{CPh}_2\cdot\text{CO}\cdot\text{NHR}$ , in which  $\text{R} = \text{H}$  (I), m.p. 144°, *Me*, m.p. 118°, *Et*, m.p. 132°, *Pr*<sup>o</sup> (II), m.p. 115°, *Bu*<sup>o</sup> (III), m.p. 112.5°, *n*-amyl, m.p. 104°, *Ph*, m.p. 180°, and *p*-*OEt*- $\text{C}_6\text{H}_4$  (IV), m.p. 121.5°.  $\text{NEt}_2\cdot\text{CPh}_2\cdot\text{CO}\cdot\text{NEt}_2$ , m.p. 67°, is similarly prepared. (I) and (IV) show 0.5–0.75 times the antispasmodic activity of 5:5-diphenylhydantoin. As an antispasmodic, (I) is most active. (II) and (III) cause contraction of isolated rabbit's intestine. R. S. C.

**Petroleum acids. VI. Naphthenic acids from Californian petroleum.** W. O. Ney, W. W. Crouch, C. E. Rannefeld, and H. L. Lochte (*J. Amer. Chem. Soc.*, 1943, **65**, 770–777; cf. A., 1943, II, 250).—Esters of high *n* yield, after purification mainly by counter-current fractional neutralisation in an improved apparatus, cyclopentanecarboxylic, 2-, b.p. 220° (*Me* ester, b.p. 165–167°; amide, m.p. 147–148°) (cf. A., 1890, 737; 1899, i, 800), and 3-methylcyclopentanecarboxylic acid, b.p. 220–224° [*amide*, m.p. 147–148°; *p*-toluidide, m.p. 106–107°; *p*-phenylphenacyl ester, m.p. 72.5–73.5° (73–74°); prepared from 3-methylcyclopentanone by  $\text{H}_2$ -Raney Ni at 100°/2200 lb. and subsequent conversion into the bromide and Grignard reagent], impure cyclohexanecarboxylic and cyclopentylacetic, 3-methyl-, and 2:3-dimethyl-cyclopentylacetic, b.p. 201–202° (*amide*, m.p. 159°; converted into and prepared from 2:3-dimethylcyclopentanecarboxylic acid), and *cis*-2:2:6-trimethylcyclohexanecarboxylic acid (gives the amide and anilide of the *trans*-acid). R. S. C.

**Isomorphous replaceability of the chalcogens in organic compounds.** H. Rheinboldt and S. Mathias (*Ber.*, 1940, **73**, [B], 433–435).— $(\text{CH}_2\cdot\text{OBz})_2$  and  $(\text{CH}_2\cdot\text{SBz})_2$  form a single eutectic without any indication of formation of mixed crystals. A continuous series of mixed crystals is given by  $\text{PhOBz}$  and  $\text{PhSBz}$  but there is no sign of such mixtures with  $\text{CO}(\text{NH}_2)_2$  and  $\text{CS}(\text{NH}_2)_2$ . H. W.

**Synthesis of isoquinoline derivatives. III. Preparation of *N*-acylvinylamines from *N*-acylaminoalcohols.** W. Krabbe, E. Polzin, and K. Culemeyer (*Ber.*, 1940, **73**, 652–655; cf. A., 1938, II, 111).— $\text{NHBz}\cdot\text{CHPh}\cdot\text{CPh}_2\cdot\text{OH}$  and  $\text{MgEtBr}\cdot\text{Et}_2\text{O}$  at 170–175° for 50–55 min. give *benz- $\alpha\beta$ -triphenylvinylamide*, m.p. 206°, converted by  $\text{HCl}\cdot\text{EtOH}$  into (?)  $\text{CPh}_2\cdot\text{CPh}\cdot\text{OH}$  and  $\text{EtOBz}$ . The analogous *Ac* derivative has m.p. 190–191°; the compound thus described (*loc. cit.*) is an oxazoline.  *$\alpha$* -Benzamido- $\beta$ -phenylpropan- $\beta$ -ol, m.p. 107–108°, prepared from  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CPhMe}\cdot\text{OH}$  and  $\text{BzCl}\cdot\text{aq. NaOH}$  or from  $\text{NHBz}\cdot\text{CH}_2\cdot\text{COMe}$  and  $\text{MgPhBr}$ , is converted by  $\text{MgEtBr}$  at 185–190° for 15 min. into *benz- $\beta$ -phenyl- $\beta$ -methylvinylamide*, m.p. 148° (corr.) (*cis*-form) (the constitution of the product, m.p. 110°, obtained by  $\text{P}_2\text{O}_5$ , is not proved).  $\text{NHBz}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{OH}$  and  $\text{MgEtBr}$  at 175° for 2 hr. give  $\text{NHBz}\cdot\text{CH}\cdot\text{CHPh}$ , m.p. 175°. A. T. P.

**Nitration of methyl 1-naphthoate and related compounds.** C. F. Koelsch and D. O. Hoffman (*J. Amer. Chem. Soc.*, 1943, **65**, 989–990).—Adding  $\text{HNO}_3$  (*d* 1.2) (3 equivs.)– $\text{H}_2\text{SO}_4$  to  $1\text{-C}_{10}\text{H}_7\cdot\text{CO}_2\text{Me}$  in  $\text{H}_2\text{SO}_4$  at 0–10° gives *Me* 4:5-dinitronaphthoate (I), m.p. 194–195° [derived acid, m.p. 266–267° (lit. 265°)], an oil, and some 5:1- and 8:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$  (formed in greater quantity if less  $\text{HNO}_3$  is used). 5:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{Me}$  is unaffected by fuming  $\text{HNO}_3\cdot\text{AcOH}$ , but with  $\text{HNO}_3$  (*d* 1.42) in  $\text{H}_2\text{SO}_4$  at 0° gives 52% of (I). *Me* 8-nitronaphthoate (prep. by  $\text{Me}_2\text{SO}_4$ ), m.p. 97–98°, and conc.  $\text{HNO}_3$  in  $\text{H}_2\text{SO}_4$  at 0–10° gives *Me* (?) 4:8-dinitronaphthoate, m.p. 189–190° [in 90%  $\text{H}_2\text{SO}_4$  at 100° gives small amounts of an acid, m.p. 236–238°, and 1:5- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$ ]. Nitration, best by fuming  $\text{HNO}_3$  in  $\text{AcOH}$ , of  $1\text{-C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$  (II) gives acids, whence  $\text{HCl}\cdot\text{EtOH}$  yields 5:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{Et}$ , whilst 8:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$  and (?) 6:8-dinitronaphthoic acid, m.p. 267–268° or (rapid heating) 274–276° [*Me* ester, m.p. 179–180°; with  $\text{Cu}(\text{OAc})_2$  in quinoline gives 1:3- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$ ], which are also formed, do not react. 5:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$  and (II) form a 1:1 additive compound, m.p. 198–200°. R. S. C.

**Textile chemistry study in the 2-hydroxynaphthoic 3-arylamide series.** H. Rath and R. Burkhardt (*Ber.*, 1940, **73**, [B], 701–708).—*p*-Nitro-*n*-dodecoanilide and  $\text{Zn}\cdot\text{AcOH}\cdot\text{EtOH}$  give *N*-dodecoyl-*p*-phenylenediamine, m.p. 112°, converted by 2:3- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{COCl}$  (I)– $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5\text{N}$  at 80° for 6 hr. into *N*-2-hydroxy-3-naphthoyl-*N'*-dodecoyl-*p*-phenylenediamine, m.p. 227–234° (the *N'*-octadecoyl analogue, m.p. 221°, is prepared similarly). *n*- $\text{C}_{11}\text{H}_{23}\cdot\text{COCl}$ –6:3:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_5\text{N}$  at 80° give 6-nitro-3-dodecoamidobenzoic acid, m.p. 133°, reduced by  $\text{Fe}\cdot\text{EtOH}\cdot\text{AcOH}$  to the 6- $\text{NH}_2$ -compound, m.p. 209°, which is then converted into 6-2'-hydroxy-3'-naphthoamido-3-dodecoamidobenzoic acid, m.p. 225° (decomp.). *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  affords *p*-2'-hydroxy-3'-naphthoamidobenzoic acid (II), m.p. ~315°. (I) and  $\text{C}_6\text{H}_5\cdot\text{AlCl}_3\cdot\text{HCl}$  at room temp., then at 60°, give 2-hydroxy-3-benzolynaphthalene (III), m.p. 155–156°. Substantivities of (II), (III), and 2:3- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{NPhR}$  ( $\text{R} = \text{Me}, \text{Et}$ ) towards viscose are < that of 2:3- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{NHPh}$ . A. T. P.

**$\alpha$ -Phenylethylidenemalononitrile.** D. T. Mowry (*J. Amer. Chem. Soc.*, 1943, **65**, 991).— $\text{CH}_2(\text{CN})_2$ ,  $\text{COPhMe}$ ,  $\text{NH}_4\text{OAc}$ , and  $\text{AcOH}$  in boiling  $\text{C}_6\text{H}_6$  with continuous removal of  $\text{H}_2\text{O}$  yield  $\alpha$ -phenylethylidenemalononitrile (56%), m.p. 94°. R. S. C.

**Ethyl  $\alpha$ :*p*-dicyanocinnamate.** D. T. Mowry (*J. Amer. Chem. Soc.*, 1943, **65**, 992).—Crude *p*- $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  [prep. from *p*- $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br}$  by aq.  $\text{Cu}(\text{NO}_3)_2$ ] with  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  and a little piperidine in  $\text{Bu}^\text{H}\text{OH}$  gives *Et*  $\alpha$ :*p*-dicyanocinnamate (88%), m.p. 168.5–169°. R. S. C.

**Attempted preparation of a homocamphor and of a 1:7-glycol.** K. Buser and H. Rupe (*Helv. Chim. Acta*, 1943, **26**, 857–863).—Gradual addition of  $\text{CHNa}(\text{CO}_2\text{Et})_2$  (I) to camphoric anhydride in boiling  $\text{C}_6\text{H}_6$  leads to "camphorylmalonic ester" [lactone of *Et*<sub>2</sub>  $\beta$ -hydroxy- $\beta$ -3-carboxy-2:2:3-trimethylcyclopentylmethylenemalonate] (II), m.p. 83–84°, in yield depending greatly on the quality of (I) and attaining 55–62% under favourable conditions. (II) is reduced ( $\text{H}_2$  at 120–130°/130 atm.—Ni catalyst in  $\text{H}_2\text{O}\cdot\text{EtOAc}\cdot\text{EtOH}$ ) to a mixture hydrolysed to  $\beta$ -3-carboxy-2:2:3-trimethylcyclopentylethane- $\alpha\alpha$ -dicarboxylic acid, m.p. 180–182° [*Me*<sub>3</sub> ester (III), b.p. 139–140°/11 mm.], and  $\beta$ -3-carboxy-2:2:3-trimethylcyclopentylpropionic acid, m.p. 141–144° [*Me*<sub>3</sub> ester (IV), b.p. 154–156°/10 mm., m.p. 35°; dichloride, b.p. 157–158°/10 mm.; *di*-*p*-toluidide, m.p. 190°]. When treated with powdered Na or  $\text{NaNH}_2$  according to Dieckmann, (III) or (IV) gives small quantities of homocamphor, m.p. 185°. Reduction of (IV) by Na and  $\text{Bu}^\text{H}\text{OH}$  affords 1:2:2-trimethyl-1-hydroxymethyl-3- $\gamma$ -hydroxy-*n*-propylcyclopentane (V), b.p. 178–180°/10 mm. (*di*-*p*-nitrobenzoate, m.p. 145°; diacetate, b.p. 189–191°/11 mm.). Replacement of OH by Br in (V) by  $\text{PBr}_3$  or  $\text{HBr}$  in  $\text{AcOH}$  could not be achieved but the action of the last reagent on the crude glycol (VI) at 160° leads to the isolation of 1:2:2-trimethyl-3- $\gamma$ -bromo-*n*-propylcyclopentane-1-carboxylic acid, m.p. 71° (*p*-toluidide, m.p. 101°), obtained by hydrolysis of the corresponding *Me* ether present in (VI). H. W.

**Mechanism of the Gattermann reaction. II.** E. L. Niedzielski and F. F. Nord (*J. Org. Chem.*, 1943, **8**, 147–152).— $\text{NaCN}$  can replace  $\text{HCN}$  in the Gattermann synthesis of aldehydes from aromatic hydrocarbons except  $\text{C}_6\text{H}_6$  in which negative polarity and lack of an alkyl substituent appear responsible for the non-formation of the aldehyde intermediate. Although *p*-xylene has a zero dipole moment it can react since it can undergo alkyl migration and alkylation by  $\text{AlCl}_3$  to form a more highly polar hydrocarbon. The yields of aldehydes from  $\text{PhMe}$  and the xylenes coincide with the polarity of the hydrocarbon reactants, the max. being reached in *o*-xylene. Compounds with labile alkyl groups, *e.g.*, *Et* and *Pr* <sup>$\beta$</sup> , show extensive alkylation and alkyl migration in the Gattermann reaction when  $\text{HCN}$  is employed. The mechanism of the  $\text{NaCN}$  and  $\text{HCN}$  actions differ. The former requires the formation of the aldehyde intermediate which appears to occur by the action of the  $\text{AlCl}_3$ -hydrocarbon complex on  $\text{NaCN}$ . During the decomp. of the  $\text{NaCN}$ , the  $\text{AlCl}_3$  displays its side reactions whereby the complete process gives products generally different from those obtained by the Gattermann reaction. Solvents exert an influence on aldehyde formation.  $\text{PhMe}$  alone gives *m*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}$  whereas in presence of  $\text{PhCl}$  as diluent, the *p*-isomeride is obtained exclusively. Dry  $\text{HCl}$  is passed through a well-stirred mixture of  $\text{AlCl}_3$ , the hydrocarbon, and  $\text{NaCN}$  for 15 min. at room temp., after which the mixture is heated to 95–100° in 20 min. and kept at this temp. The following are new: diethylbenzaldehyde, b.p. 115–118°/9 mm. (2:4-dinitrophenylhydrazones, m.p. 132°), converted into the corresponding acid, m.p. 81° (*amide*, m.p. 161°), and hydantoin, m.p. 175°; triethylbenzaldehyde, b.p. 138–140°/9 mm. (*semicarbazone*, m.p. 151°; 2:4-dinitrophenylhydrazones, m.p. 162°; corresponding acid, m.p. 111°); diisopropylbenzaldehydes, b.p. 135–139°/9 mm., 126–130°/9 mm., and 126–134°/9 mm. (2:4-dinitrophenylhydrazones, m.p. 143°, 120°, and 133°; corresponding acids, m.p. 190°, 181°, and 186°, respectively); triisopropylbenzaldehydes, b.p. 129–133°/9 mm. and 145–152°/9 mm. (2:4-dinitrophenylhydrazones, m.p. 169° and 151°; acids, m.p. — and 182°, respectively); methyl-diisopropylbenzaldehydes, b.p. 133–138°/14 mm. and 142–150°/14 mm. (2:4-dinitrophenylhydrazones, m.p. 129° and 157°; acids, m.p. 121° and 125°, respectively). H. W.

**Fries rearrangement and subsequent isomerisation.** G. Baddeley (*J.C.S.*, 1943, 273–274).—3:5:1- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{O}\cdot\text{COR}$  ( $\text{R} = \text{Me}, \text{Et}, \text{Ph}$ ) are converted quantitatively by 1 mol. of  $\text{AlCl}_3$  into 6:2:4:1- $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{COR}$  (I) but by 2 or more mols. into 6:3:4:1- $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{COR}$  (II); migration of one alkyl is thus not conditioned by another alkyl in the *p*-position to it (cf. von Auwers *et al.*, A., 1928, 417). With <2 mols. of  $\text{AlCl}_3$ , (I) similarly give (II); the reaction is bimol. Other similar examples are quoted. 6-Hydroxy-3:4-dimethyl-propiophenone, m.p. 60°, and -benzophenone, m.p. 111°, 6-hydroxy-2:4-dimethylpropiophenone, m.p. 78°, dibromo-6-hydroxy-2:4-, m.p. 81°, and bromo-6-hydroxy-3:4-diethylacetophenone, m.p. 59°, are new. F. R. S.

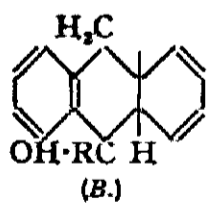
**Vinyl alcohols. VI. 1:4-Dehydrogenation.** R. C. Fuson and R. E. Foster. **VII. Hindrance at the  $\beta$ -carbon atom.** R. C. Fuson and Q. F. Soper (*J. Amer. Chem. Soc.*, 1943, **65**, 913–915, 915–917; cf. A., 1943, II, 160).—VI. Hydrogenation of  $\text{CHAr}\cdot\text{CAR}\cdot\text{COAr}'$  (A), in which  $\text{Ar}'$  is highly hindered, gives an enol,  $\text{CH}_2\text{Ar}\cdot\text{CAR}\cdot\text{CAR}'\cdot\text{OH}$ , which is immediately oxidised to (A) in air but when kept ketonises to give  $\text{CH}_2\text{Ar}\cdot\text{CHAr}\cdot\text{COAr}'$ . Duryl

$\text{CH}_2\text{Ph}$  ketone (prep. from durene and  $\text{CH}_2\text{Ph}\cdot\text{COCl}$  by Friedel-Crafts reaction), m.p. 110—111°, with  $\text{PhCHO}$  and 10%  $\text{NaOH}$  in  $\text{EtOH}$  at room temp. gives *duryl*  $\alpha\beta$ -diphenylvinyl ketone (I) (70%), m.p. 150—151°. When (I) is hydrogenated ( $\text{PtO}_2$ ) in  $\text{EtOAc}$  and the solvent is removed in air, only (I) is recovered, but keeping the reduced solution for 48 hr. or boiling it for 2 hr. under  $\text{N}_2$  leads to *duryl*  $\alpha\beta$ -diphenylethyl ketone (II), m.p. 106—107°. Hydrogenation in presence of  $\text{ZnCl}_2$  in  $\text{Ac}_2\text{O}$  does not give an enol acetate and (I) gives no peroxide.  $\text{Na-EtOH}$  reduces (I) to (II). Hydrogenation of 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Pr}_3$   $\alpha\beta$ -diphenylvinyl ketone, m.p. 117—119°, *duryl*, m.p. 138—140°, and *mesityl*  $\alpha$ -phenyl- $\beta$ -p-chlorophenylvinyl ketone, m.p. 138—140°, gives similar results. 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Pr}_3$   $\text{CH}_2\text{Ph}$  (III), m.p. 60.5—61°, and  $\alpha\beta$ -diphenylethyl ketone, m.p. 143—144°, *duryl*, m.p. 129—130°, and *mesityl*  $\alpha$ -phenyl- $\beta$ -p-chlorophenylethyl ketone, m.p. 148—149°, are described.

VII. The stability of unchelated enols is due to steric conditions at  $\text{C}_{(B)}$  rather than at  $\text{C}_{(A)}$ . In the Grignard machine, (III) gives nearly 1 mol. of  $\text{CH}_4$  but then regenerates (III).  $\text{CHPhMe}\cdot\text{COCl}$  (modified prep.), b.p. 75—76°/3 mm., with  $s\text{-C}_6\text{H}_3\text{Pr}_3$  and  $\text{AlCl}_3$  in  $\text{CS}_2$ , at, successively, 0°, room temp., and the b.p. gives 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Pr}_3$   $\text{CHPhMe}$  ketone, m.p. 83—84°, which does not enolise in  $\text{NaOEt-EtOH}$  or give an enol acetate or benzoate, shows 1 active H, and with  $\text{SeO}_2$  in boiling dioxan containing a little  $\text{H}_2\text{O}$  yields *Ph* 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Pr}_3$  diketone (IV), m.p. 121.5—122.2°.  $\text{H}_2\text{-Cu}$  chromite reduces (IV) at 175°/2000 lb. to  $\alpha$ -phenyl- $\beta$ -2 : 4 : 6-triisopropylphenylethylene glycol, m.p. 133.5—134° (diacetate, m.p. 113—114°; dehydrated by conc.  $\text{HCl-AcOH}$  to an intractable product), but at 150°/1500—2000 lb. to 2 : 4 : 6-triisopropylbenzoylphenylcarbinol (V), m.p. 117.5—118.5° (acetate, m.p. 120—120.5°), also obtained by  $\text{Zn dust-HCl-EtOH}$ . Hydrogenation of (IV) gives an enediol (indophenol test), which, however, could not be isolated;  $\text{H}_2\text{-PtO}_2$ -conc.  $\text{HCl}$  (3 drops)- $\text{ZnCl}_2\text{-Ac}_2\text{O}$  gives  $\alpha\beta$ -diacetoxy- $\alpha$ -phenyl- $\beta$ -2 : 4 : 6-triisopropylphenylethylene, m.p. 161—161.5°, hydrolysed by  $\text{HCl-MeOH-H}_2\text{O}$  to (V); hydrogenation in light petroleum or  $\text{Et}_2\text{O}$  and exposure to air gives (IV) or (V), respectively. M.p. (both parts) are corr. R. S. C.

Acetylation of deoxybenzoins. R. P. Barnes, S. R. Cooper, V. J. Tulane, and H. Delaney (*J. Org. Chem.*, 1943, 8, 153—158).—The mechanism presented (A., 1941, II, 170) for the benzoin rearrangement is applied to the acetylation of deoxybenzoins. *Ph* *p*-methoxybenzyl ketone, m.p. 98°, is obtained from the corresponding phenol,  $\text{Me}_2\text{SO}_4$ , and  $\text{NaOH}$ . The following are prepared by heating the necessary deoxybenzoin (A) with twice its wt. of  $\text{KOAc}$  and sufficient boiling  $\text{Ac}_2\text{O}$  to dissolve the latter :  $\alpha$ -acetoxy- $\alpha\beta$ -diphenyl-, m.p. 101°;  $\alpha$ -acetoxy- $\alpha\beta$ -diphenyl- $\beta$ -benzyl-, m.p. 70°;  $\alpha$ -acetoxy- $\beta$ -phenyl- $\alpha$ -p-acetoxyphenyl-, m.p. 109°;  $\alpha$ -acetoxy- $\alpha$ -phenyl- $\beta$ -p-acetoxyphenyl-, m.p. 119°;  $\alpha$ -acetoxy- $\alpha\beta$ -triphenyl-, m.p. 104°;  $\alpha$ -acetoxy- $\alpha\beta$ -dimesityl-, m.p. 106°;  $\alpha$ -acetoxy- $\beta$ -phenyl- $\alpha$ -p-anisyl-, m.p. 88°;  $\alpha$ -acetoxy- $\alpha$ -phenyl- $\beta$ -p-anisyl-, m.p. 86°;  $\alpha$ -acetoxy- $\alpha\beta$ -di-p-anisyl-, m.p. 90°;  $\alpha$ -acetoxy- $\alpha$ -phenyl- $\beta$ -p-nitrophenyl-, m.p. 107°;  $\alpha$ -acetoxy- $\alpha$ -phenyl- $\beta$ -p-acetamidophenyl-, m.p. 137°, -ethylene. These are hydrolysed ( $\text{EtOH-HCl}$ ) smoothly to (A). H. W.

Aromatic cyclodehydration. XI. Mechanism of the cyclisation of *o*-benzylphenones [*o*-benzylphenyl ketones]. C. K. Bradsher and E. S. Smith (*J. Amer. Chem. Soc.*, 1943, 65, 854—857; cf. Berliner, A., 1943, II, 141).—Cyclisation of *o*- $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{COR}$  (A) is held to proceed by addition of  $\text{H}^+$  to give an ion containing  $\cdot\text{C}^+\text{R}\cdot\text{OH}$ ,



cyclisation to (B), loss of  $\text{H}^+$  to give the anthranol, and dehydration thereof to the 9-substituted anthracene. The reasons are that cyclisation is slower than in the phenanthrene series, that the rate is independent of the nature of R, and because of the following reactions. *o*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{COPh}$  with boiling 48%  $\text{HBr}$  ( $\text{HBr-AcOH}$  gives a resin) and then  $\text{EtOH}$  gives 9-ethoxy-9-phenylfluorene (65%), m.p. 114—115°; (A; R = Ph) is similarly cyclised in 66% yield to 9-phenylanthracene. *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CPh}_2\text{Cl}$  (improved prep.) with  $\text{MgMeI}$  in  $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$  gives *o*-chloro- (26%), m.p. 107.5—108.5°, which with  $\text{CuCN}$  in  $\text{C}_5\text{H}_5\text{N}$  at 215—225° gives *o*-cyano-*aaa*-triphenylethane (43%), m.p. 123—124°. This resists acid or alkaline hydrolysis, but with  $\text{MgPhBr-Et}_2\text{O}$  and then  $-\text{C}_6\text{H}_5$  at the b.p. gives *o*- $\alpha$ -methylbenzhydrylbenzophenoneimine hydrochloride (83.5%), which with boiling 48%  $\text{HBr}$  and then dry  $\text{ROH}$  yields 10-ethoxy- (57%), m.p. 203—204°, and 10-methoxy-9 : 10-diphenyl-9-methyl-9 : 10-dihydroanthracene, m.p. 284—286°. Substitution of Ar into the  $\text{CH}_2$  of (A) slows the cyclisation; enolisation plays no part in the mechanism. R. S. C.

*tert*-Butyl benzoylisobutyrate. J. C. Shivers and C. R. Hauser (*J. Amer. Chem. Soc.*, 1943, 65, 991).— $\text{Pr}^i\text{CO}_2\text{Bu}^t$  with  $\text{CPh}_3\text{Na}$  and then  $\text{BzCl}$  in  $\text{Et}_2\text{O}$  gives  $\text{Bu}^t$   $\alpha$ -benzoylisobutyrate, m.p. 64—65°, b.p. 146—148°/15 mm. R. S. C.

Photo-reactions. V. Photo-oxidation of non-ionisable thioketones in sunlight. A. Schönberg and A. Mostafa (*J.C.S.*, 1943, 275—276).— $\text{CSPH}_2$  is converted by  $\text{O}_2$  into  $\text{COPH}_2$  even in the dark. (*p*- $\text{C}_6\text{H}_4\text{R}$ ) $_2\text{CS}$  (R =  $\text{OMe}$ ,  $\text{NMe}_2$ ), xanthione, and thioxanthione in  $\text{C}_6\text{H}_6$  are stable to  $\text{O}_2$  in the dark but give the corresponding ketones in sunlight, S and  $\text{SO}_2$  being formed; *N*-phenylthioacridone, 4-

thioflavone, and 2 : 6-diphenyldithiopyrone are stable in dark and sunlight. F. R. S.

Alkylcyclohexanones.—See B., 1943, II, 245.

Preparation of synthetic sex hormones. II. Derivatives of hexoestrol. J. F. Lane and E. S. Wallis (*J. Amer. Chem. Soc.*, 1943, 65, 994; cf. A., 1941, II, 9).—Mixed mono- and di-acetates of perhydrohexoestrol (m.p. 167°) with  $\text{CrO}_3\text{-AcOH}$  and then  $\text{NaOH-EtOH}$  give, after purification by way of the H succinates, 4-hydroxy-4'-keto-, m.p. 70° [semicarbazone, m.p. 146°; acetate, m.p. 66° (semicarbazone, m.p. 161°)], and a little 4 : 4'-diketo- $\gamma\delta$ -dicyclohexyl-*n*-hexane, m.p. 80°. R. S. C.

Action of acids on 2 : 3-epoxy-2 : 3-diphenylindanone. C. F. Koelsch and C. D. Le Claire (*J. Amer. Chem. Soc.*, 1943, 65, 754—755).—2 : 3-Epoxy-2 : 3-diphenylindan-1-one (I) with a drop of  $\text{H}_2\text{SO}_4$  in warm  $\text{AcOH}$  gives yellow 3 : 4-diphenylisocoumarin (II), m.p. 168—169° (Weitz *et al.*, A., 1921, i, 869, m.p. 168.5—171°), the structure of which is proved by hydrolysis by warm  $\text{NaOH-EtOH}$  to *o*- $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{COPh}$  (III) and by boiling  $\text{NaOH-MeOH-H}_2\text{O}$  to  $\text{BzOH}$  and *o*- $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ . Boiling 2%  $\text{H}_2\text{SO}_4\text{-AcOH}$  cyclises (III) to colourless (II), the original colour of which is thus due to impurities. With  $\text{AcOH-HCl}$  at room temp. (5 min.), (I) gives 2 : 3-dihydroxy-2 : 3-diphenylindan-1-one, sinters 160°, m.p. 168° (cf. *loc. cit.*) [and a little (II)], the structure of which is shown by oxidation by  $\text{Pb(OAc)}_4$  in warm  $\text{C}_6\text{H}_6$  to *o*-benzoylbenzil, m.p. 93—94° (also obtained from diphenylindone by  $\text{CrO}_3\text{-AcOH}$  at 80—85°). The compound obtained from 2 : 3-epoxy-3-*p*-dimethylaminophenyl-2-*o*-formylphenylindan-1-one by acid (Weitz, A., 1919, i, 290) is similarly 4-*p*-dimethylaminophenyl-3-*o*-formylphenylisocoumarin. R. S. C.

Alkamine esters of fluorenonecarboxylic acids. F. E. Ray and G. Rieveschl, jun. (*J. Amer. Chem. Soc.*, 1943, 65, 836—839).—Condensing fluorene with  $\text{Ac}_2\text{O-AlCl}_3$  in boiling  $\text{CS}_2$  and oxidising the crude product with  $\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$  (later +  $\text{Ac}_2\text{O}$ ) gives 58—62% of fluorenone-2-carboxylic acid (I), m.p. 339—341° [Me ester, m.p. 185—186° (lit. 181°)], and 2-acetylfluorenone, m.p. 154—155°. With  $\text{Zn dust}$  in  $\text{KOH-EtOH-H}_2\text{O}$ , (I) gives fluorenol-2-, sinters 224—240°, and thence by red  $\text{P-I-AcOH}$  fluorene-2-carboxylic acid, m.p. 262—267° (lit. 260°) (decomp.) [Me ester, m.p. 122° (lit. 120°)]. Fluorenone-2-, m.p. 183—184°, -1-, m.p. 130—132° (lit. 140°), and -4- [acid, m.p. 227° (lit. 223—224°)], and fluorene-2-carboxyl chloride, m.p. 182°, with the appropriate  $\text{NH}_2$ -alcohol give  $\beta$ -diethylaminoethyl fluorenone-1-, m.p. 194—195°, -4-, m.p. 194—196°, and -2- (II), m.p. 223—224°, and fluorene-2-carboxylate hydrochloride, m.p. 204—206°,  $\gamma$ -diethylamino-*n*-propyl fluorenone-1-, m.p. 159—160°, -4-, m.p. 210—211°, and -2-carboxylate hydrochloride (III), m.p. 221—224°,  $\beta$ -dibutyl-, m.p. 179—180°, and  $\beta$ -dimethylaminoethyl fluorenone-2-carboxylate hydrochloride, m.p. 222—224°. With  $\text{NH}_2\text{OH, HCl}$  and  $\text{BaCO}_3$  in boiling  $\text{MeOH}$ , (II) and (III) give the oxime hydrochloride, m.p. 231—232°, and oxime dihydrochloride, m.p. 219—220°, respectively, which are more potent anaesthetics than are the parent esters. R. S. C.

Ring-enlargement of 2 : 4 : 5-triphenylcyclopentenedione. C. F. Koelsch and S. Wawzonek (*J. Amer. Chem. Soc.*, 1943, 65, 755—757).—2 : 4 : 5-Triphenyl- $\Delta^4$ -cyclopentene-1 : 3-dione (A., 1942, II, 23),  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ , and  $\text{NaOEt}$  in boiling  $\text{EtOH}$  give *Et* 2 : 5-diketo-1 : 3 : 4-triphenyl- $\Delta^3$ -cyclopentenylacetate (74%), m.p. 126—127°, converted by boiling  $\text{NaOEt-EtOH-H}_2$  into *Et* 3 : 4 : 6-triphenylgentisate (I) (76%), m.p. 155—157° (diacetate, m.p. 157—159°). The derived ( $\text{KOH-H}_2\text{O-EtOH}$ ) acid (II), m.p. 216—221° (gas), with a trace of  $\text{Cu(OAc)}_2$  in boiling quinoline- $\text{H}_2$  gives triphenylquinol (55%) (III), m.p. 151—152° (1 : 1 additive compound, m.p. 188—192°, with quinoline hydrochloride), oxidised by  $\text{CrO}_3\text{-AcOH-H}_2\text{O}$  to triphenyl-*p*-benzoquinone, m.p. 154.5—155°. This is reduced to (III) by  $\text{Zn dust}$  in  $\text{AcOH}$  and with  $\text{PhN}_2\text{Cl}$  in aq.  $\text{AcOH-NaOAc}$  at 10° gives a little 1 : 2 : 3 : 5 : 6 : 4- $\text{O}^-\text{C}_6\text{H}_4\cdot\text{O}$ . Boiling  $\text{CrO}_3\text{-AcOH}$  oxidises (I) to *Et* triphenyl-*p*-benzoquinonecarboxylate, m.p. 207—208°, converted into (II) by  $\text{KOH-H}_2\text{O-EtOH}$ .  $\text{FeCl}_3\text{-AcOH-H}_2\text{O}$  ( $\text{CrO}_3$  and  $\text{PbO}_2$  give complex products) oxidises (II) to triphenyl-*p*-benzoquinonecarboxylic acid (55%), m.p. 213—215° (decomp.) [202—207° (decomp.)]. Passing air into (I) in  $\text{KOH-EtOH-H}_2\text{O}$  gives 2-hydroxy-3 : 5 : 6-triphenyl-*p*-benzoquinone, m.p. 160—161.5° (acetate, m.p. 185.5—187.5°). R. S. C.

Synthesis of 2 : 6-diphenylcyclooctane-1 : 5-dione. S. Wawzonek (*J. Amer. Chem. Soc.*, 1943, 65, 839—843).—dicyclo[3, 0, 3]Octane-2 : 6-dione (Ruzicka *et al.*, A., 1934, 297) with  $\text{PCl}_5\text{-C}_6\text{H}_6$ ,  $\text{SeO}_2\text{-EtOH}$ , or 2 : 4 : 6 : 1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{MgBr}$  and then I in  $\text{Et}_2\text{O-EtOH}$  gives intractable products, but with  $\text{MgPhBr}$  in  $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$  and then aq.  $\text{NH}_4\text{Cl}$  gives 2 : 6-dihydroxy-2 : 6-diphenyldicyclo[3, 0, 3]octane, m.p. 208—212° (decomp.) (chromophoric salts with  $\text{H}_2\text{SO}_4$  or  $\text{HCl-AcOH}$ ; OH and H *cis*), which with  $\text{H}_2\text{SO}_4\text{-MeOH}$  at room temp. gives the *Me*<sub>2</sub> ether, m.p. 174—175°, and with  $\text{KHSO}_4$  at 150—160° or, better, boiling  $\text{AcOH-HCO}_2\text{H}$  gives 2 : 6-diphenyldicyclo[3, 0, 3]- $\Delta^2$ -*s*-octadiene (I), m.p. 136—138°.  $\text{MgMeI}$  gives similarly 2 : 6-dihydroxy-2 : 6-dimethyldicyclo[3, 0, 3]octane, m.p.

133—135°, but dehydration thereof gives an unstable terpene-like oil. The structure of (I) is proved by oxidation by  $\text{CrO}_3\text{--NaHSO}_4\text{--H}_2\text{O}$  at 100° to  $\beta\beta'$ -dibenzoyladipic acid, m.p. 186—188° (gas), which is also obtained [m.p. 189—190° (gas)] from 4:5-dibenzoyl- $\Delta^1$ -cyclohexene by  $\text{CrO}_3\text{--AcOH}$  at 100°. Boiling  $n\text{-C}_6\text{H}_{11}\text{ONa}\text{--C}_6\text{H}_{11}\text{OH}$  does not affect (I), but  $p\text{-C}_6\text{H}_4\text{Me}\text{SO}_3\text{H}$  (II) in boiling  $\text{C}_6\text{H}_6$  partly rearranges it to 2:6-diphenyldicyclo[3, 0, 3]- $\Delta^1$ :5-octadiene (III), m.p. 188—190°, the structure of which is proved by conversion by  $\text{O}_3$  in EtOAc at  $-40^\circ$  into a dioxonide, m.p. 122—127° (gas), which with  $\text{H}_2\text{--PtO}_2$  at 2.7 atm. gives  $\alpha\theta$ -diphenyl-n-octane- $\alpha\delta\theta$ -tetraone, m.p. 110—111° (quinoxaline derivative, m.p. 166.5—167.5°), and  $\text{Bz}\cdot[\text{CH}_2]_6\cdot\text{CO}_2\text{H}$ . With  $\text{H}_2\text{--Pt}$  or  $\text{--Pd}$  in EtOAc, (I) or (III) gives 2:6-diphenyldicyclo[3, 0, 3]octane (IV), m.p. 110—112°, but with  $\text{Br}\text{--CCl}_4$  at 0° gives unstable oils. 40%  $\text{Na}\text{--Hg}$  in  $\text{C}_6\text{H}_6\text{--EtOH}$  (not other metal reductants) reduces (III) to 2:6-diphenyldicyclo[3, 0, 3]- $\Delta^{1(5)}$ -octene (V), m.p. 115—116°, which with  $\text{H}_2\text{--PtO}_2$  in EtOH gives a diphenyldicyclooctane, m.p. 99—100° [isomeric with (IV)], with  $\text{Br}$  gives an unstable product, is unaffected by a dropping  $\text{Hg}$  electrode in 0.175M- $\text{NBu}_4\text{I}\text{--}75\%$  dioxan, and with (II) in boiling xylene (not  $n\text{-C}_5\text{H}_{11}\text{ONa}$ ) gives 2:6-diphenyldicyclo[3, 0, 3]- $\Delta^2$ -octene, m.p. 106—108° (reduced at a dropping  $\text{Hg}$  electrode). With  $\text{O}_3$  in EtOAc at  $-40^\circ$  and then  $\text{H}_2\text{--PtO}_2$  at 2 atm., (V) gives 2:6-diphenylcyclooctane-1:5-dione (VI), m.p. 217—220° (dioxime, softens 140°, m.p. 148—150°), and other products including isomericides. With  $\text{PCl}_5$  in boiling xylene, (VI) yields 1:5-dichloro-2:6-diphenyl- $\Delta^{1:5}$ -cyclooctadiene, m.p. 187—188°, with  $\text{Zn}$  dust in boiling 90%  $\text{AcOH}$  gives 1:5-dihydroxy-2:6-diphenyldicyclo[3, 0, 3]octane, m.p. 127—129° [with  $\text{KHSO}_4$  at 150—160° gives an oil; converted by  $\text{Pb}(\text{OAc})_4\text{--C}_6\text{H}_6$  at 47° into (VI)], and with boiling  $\text{Ac}_2\text{O}\text{--(II)}$  (not  $\text{--KOAc}$  or  $\text{--H}_2\text{SO}_4$ ) gives 5-acetoxy-2:6-diphenyl- $\Delta^5$ -cyclooctenone, m.p. 123—124°.

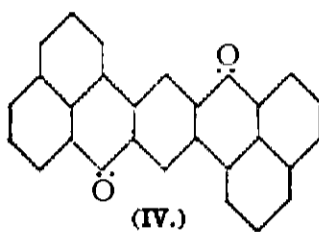
R. S. C.

**Action of acid anhydrides on acenaphthenone.** E. Ghigi (*Ber.*, 1940, 73, [B], 677—700).—Acenaphthenone (I) and boiling  $\text{Ac}_2\text{O}\text{--NaOAc}$  (10 hr.) give 7-acetoxy-8-acetylacenaphthylene (II), m.p. 133—134°, which is oxidised by  $\text{KMnO}_4$  in  $\text{C}_6\text{H}_6$  to 1:8- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$  (III) or by cold  $\text{CrO}_3$  to (III) and a little acenaphthenequinone. (II) and aq.  $\text{NaOH}$  yield the corresponding 7-OH-compound (IV), m.p. 117° [ $\text{Na}$ ,  $\text{Fe}^{\text{III}}$ , and  $\text{Cu}$  salts; *Me ether* m.p. 131—132° ( $\text{CH}_2\text{N}_2$ ); *benzoate*, m.p. 148—149°; *phenylhydrazone*, m.p. 196—198°, and thence 4:5-1':8'-naphthylene-1-phenyl-3-methylpyrazole, m.p. 103°; *p-nitrophenylhydrazone*, m.p. 206—207° (decomp.), and corresponding *pyrazole*, m.p. 247°; *oxime*, m.p. 201—203°; *semicarbazone*, m.p. 235—236° (decomp.)], with a considerable amount of diacenaphthylidene (V). (I) and  $\text{Ac}_2\text{O}\text{--C}_5\text{H}_5\text{N}$  at room temp. for 4 days give a little diacenaphthylidenedione (VI), a product, m.p. 225—235°, and the compound, (II) +  $\text{C}_5\text{H}_5\text{N}$ , m.p. 145—147°. (IV) with  $\text{Na}_2\text{Cr}_2\text{O}_7\text{--AcOH}$  at 85°, or aq.  $\text{KMnO}_4\text{--NaOH}$ , or aq.  $\text{H}_2\text{O}_2$  at 100° (bath), gives 1:8- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$ . Other reactions of (IV) are: with boiling  $\text{Pb}(\text{OAc})_4\text{--C}_6\text{H}_6$ , it gives a compound, m.p. 215—220° (decomp.); with  $\text{KOH}$  at 250°, 8:1- $\text{C}_{10}\text{H}_6\text{Me}\text{CO}_2\text{H}$ , m.p. 152—153° (lit. 130—131°); with  $\text{PhN}_2\text{Cl}\text{--aq. KOH}\text{--EtOH}$ , acenaphthenequinonephenylhydrazone; with  $\text{MgPhBr}\text{--Et}_2\text{O}$ , it yields (I) and  $\text{COPhMe}$ ; with  $\text{MgMeI}\text{--Et}_2\text{O}$ , (probably) the inner ether, m.p. 74—75°, of 7-hydroxy-8- $\alpha$ -hydroxyisopropylacenaphthylene; with  $\text{Zn}$  dust, acenaphthene is formed; with  $\text{Cu}\text{--quinoline}$ , (I); with 20% aq.  $\text{NaOH}$  or  $\text{HCl}\text{--MeOH}$ , (V); with  $\text{Br}$ , dibromoacenaphthenone, m.p. 161—162°; other (largely negative) reactions of (IV) are given.  $\text{Mg}$  acenaphthenonyl bromide [from monobromoacenaphthenone (VII) and  $\text{Mg}\text{--xylene}$ ] with cold  $\text{AcCl}$  yields (VI) and 7:7'-diacenaphthenonyl; the latter is also obtained from (VII)– $\text{Mg}\text{--EtOAc}$  (trace of I). (II) and  $\text{AlCl}_3$  at 140° yield (probably) 7-hydroxy-4:8-diacetylacenaphthylene (VIII), m.p. 166—167° (*bisphenylhydrazone*, m.p. 233°; *acetate*, m.p. 175°), oxidised by aq.  $\text{KMnO}_4\text{--NaOH}$  or  $\text{CrO}_3$  to 4-acetyl- and 4-carboxy-naphthalic anhydride. (VIII) and  $\text{PhN}_2\text{Cl}\text{--aq. NaOH}\text{--EtOH}$  afford 4-acetylacenaphthenequinone-8-monophenylhydrazone, m.p. 215°. (I) and  $\text{Bz}_2\text{O}\text{--NaOBz}$  at 160° yield 7-benzoyloxy-8-benzoylacenaphthylene, forms m.p. 145° and 202—203°, hydrolysed (best by alkali) to 7-hydroxy-8-benzoylacenaphthylene (IX), m.p. 100° (*acetate*, m.p. 163°; *pyrazole*, m.p. 193—194°, from  $\text{NHPh}\cdot\text{NH}_2$ ). (IX) with  $\text{PhN}_2\text{Cl}$  gives acenaphthenequinonephenylhydrazone, with boiling  $\text{Ac}_2\text{O}\text{--NaOAc}$  yields (II), with  $\text{KOH}$  at 250° affords 8:1- $\text{C}_{10}\text{H}_6\text{Me}\text{CO}_2\text{H}$ , with  $\text{H}_2\text{SO}_4$  at 150—160° gives (VI), and by Clemmensen reduction, a product, m.p. 190—192°. (I)– $\text{NaNH}_2\text{--BzCl}$  afford small amounts of (III), (IX), and (V) [also from (I)– $\text{KCN}\text{--MeOH}$ ]. (I) and  $\text{MgPhBr}\text{--Et}_2\text{O}$  yield (probably) 7-phenylacenaphthylene, m.p. 54—55°, oxidised by  $\text{CrO}_3\text{--AcOH}$  to 1:8- $\text{C}_{10}\text{H}_6\text{Bz}\cdot\text{CO}_2\text{H}$ , m.p. 131—132° (lit. 110—112°). A. T. P.

**Highly arylated aromatic compounds. X. Action of quinones on phenacyclone.** W. Dilthey and M. Leonhard (*Ber.*, 1940, 73, [B], 430—432).—Phenacyclone (I) and 1:4- $\text{O}\cdot\text{C}_{10}\text{H}_6\cdot\text{O}$  in boiling  $\text{PhCl}$  and  $\text{CO}_2$  give 1:4-endo-carbonyl-1:4-diphenyl-2:3-diphenylene-1:4:11:12-tetrahydroanthraquinone (II), m.p. 287—288° (decomp.) after darkening (lit. 265—267°) (preheated to 280°), slowly converted by  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in boiling  $\text{C}_6\text{H}_5\text{N}$  into 1:4-diphenyl-2:3-diphenylene-11:12-dihydroanthraquinone, m.p. 334—335° (bath heated to 330°), which passes in  $\text{C}_6\text{H}_5\text{N}$  containing a little  $\text{KOH}\text{--MeOH}$  into 1:4-diphenyl-2:3-diphenyleneanthraquinone, m.p. 376°

(lit. 359°), also obtained from (II) and  $\text{CrO}_3\text{--AcOH}$  or boiling  $\text{C}_6\text{H}_5\text{N}$  (3 days). 1:4-endo-carbonyl-1:4-diphenyl-2:3-diphenylene-1:4:9:10-tetrahydronaphtha-5:8-quinone has m.p. 260—262° (decomp.) (lit. 194°) (bath preheated to 245°). Naphthazarin and (I) in boiling anhyd.  $\text{C}_6\text{H}_6$  and  $\text{CO}_2$  afford 5:8-endo-carbonyl-5:8-diphenyl-6:7-diphenylene-13:14-dihydroquinizarin, m.p. 245° (decomp.) [*diacetate*, m.p. 265° (decomp.)], also obtained from (I) and diacetylnaphthazarin]. H. W.

**Aromatic hydrocarbons and their derivatives. XXXI. Syntheses in the pentacene series.** E. Clar (*Ber.*, 1940, 73, [B], 409—415).—Reduction of pentacenequinones does not give quinols but invariably leads to further reduction products. *leuco*Quinizarin and  $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$  at 280—300° give 5:7:12:14-tetrahydroxypentacene-6:13-quinone (I), reduced by  $\text{Zn}$  dust and 70%  $\text{AcOH}$  in boiling  $\text{C}_6\text{H}_5\text{N}$  containing a little  $\text{CuSO}_4$  to 5:7:12:14-tetrahydroxy-6:13-dihdropentacene-6-one (II), which is readily oxidised by air and best isolated as the *tetra-acetate*, becomes violet-red at 230°, commences to melt at 255°, and darkens with evolution of gas at 280°. (II) is reduced by  $\text{Zn}$  dust and boiling dil.  $\text{NaOH}$  to 5:7:12:14-tetrahydroxy-6:13-dihdropentacene (III), m.p.  $\sim 315^\circ$  (decomp.), softens at 230° in a sealed capillary (*tetra-acetate*, becomes brown at 270°, m.p.  $>370^\circ$ ); direct reduction of (I) to (III) by  $\text{Zn}$  dust and  $\text{NaOH}$  is very slow. (III) loses  $\text{H}_2\text{O}$  at  $>200^\circ/\text{vac.}$  in  $\text{CO}_2$  and forms *pentacene-5:12-quinone*, m.p. 310—315° (decomp.), darkens and softens at 280° in a sealed capillary, which does not give a vat. (III), glycerol, and  $\text{H}_2\text{SO}_4$  at 120—125° give 1:14-7:8-dibenzopentacene-5:12-quinone (IV), m.p.  $>370^\circ$ , converted by



$\text{NaCl}$ , somewhat moist  $\text{ZnCl}_2$ , and  $\text{Zn}$  dust at 210° into 3:3'-7:3'-di(trimethylene)-1:2-5:6-dibenzanthracene, m.p. 255—256°.

H. W.

## IV.—STEROLS AND STEROID SAPOGENINS.

### Preparation of cholestenes, cholestadienes, and cholestatrienes.

E. W. Hollingsworth (*Iowa State Coll. J. Sci.*, 1942, 17, 80—81).—A summary of work previously abstracted (A., 1941, II, 92; 1942, II, 25, 137, 167). Dehydration of  $\Delta^4$ :6-cholestadien-3-ol and  $\Delta^3$ :5-cholestadien-7-ol probably yields  $\Delta^2$ :4:6- and  $\Delta^3$ :5:7-cholestatriene, respectively.

F. R. G.

**Product of irradiation of  $\Delta^6$ :8-coprostadienol.** G. Zühlsdorff (*Ber.*, 1940, 73, [B], 328—331; cf. A., 1939, II, 18).—Exposure of  $\Delta^6$ :8-cholestadienol [giving first  $\Delta^6$ :8-coprostadienol (I)] in  $\text{C}_6\text{H}_6$  to a  $\text{Mg}$  spark light affords (I) and photocholestadienol-2 (II), m.p. 104°,  $[\alpha]_D^{25} + 280^\circ$  (3:5-dinitrobenzoate, m.p. 151°), which is isomeric with (I), contains two unconjugated double linkings, and gives no insol. digitonide. With  $\text{Se}$  at 330°, (II) affords unidentified oils and a trace of cryst. solid, m.p. 190°. Dehydrogenation of (II) with  $\text{Al}(\text{O}i\text{Bu})_3\text{--COMe}_2$  gives an oily ketone [*semicarbazone*,  $\text{C}_{28}\text{H}_{44}\text{ON}_3$ , m.p. 231—232° (decomp.),  $[\alpha]_D^{18} - 13.8^\circ$ ]. (II) and  $\text{H}_2\text{--Pt}\text{--black}\text{--AcOH}$  yield a  $\text{H}_2$ -derivative, m.p. 88—90°,  $[\alpha]_D^{17} + 55.2^\circ$ , purified through its 3:5-dinitrobenzoate, m.p. 181°,  $[\alpha]_D^{16} + 53^\circ$ . (II) and  $\text{HCl}\text{--CHCl}_3$  give an isomeride, m.p. 136°,  $[\alpha]_D^{20} - 64.5^\circ$  (3:5-dinitrobenzoate, m.p. 147—148°,  $[\alpha]_D^{21} + 5.85^\circ$ ; *acetate*, m.p. 92°,  $[\alpha]_D^{20} - 35^\circ$ ; no digitonide), which contains conjugated double linkings and is hydrogenated to a  $\text{H}_2$ -compound (3:5-dinitrobenzoate, m.p. 112—113°,  $[\alpha]_D^{21} + 18.2^\circ$ ).  $[\alpha]$  are in  $\text{CHCl}_3$ .

A. T. P.

**$\Delta^{11}$ -Dehydroneoergosterol.** A. Windaus and C. Roosen-Runge (*Ber.*, 1940, 73, [B], 321—325).—Irradiation (sunlight) of dehydroergosteryl acetate in  $\text{EtOH}\text{--C}_6\text{H}_6\text{--eosin}$  in absence of air gives a bimol. diacetate, m.p. 194°,  $[\alpha]_D^{19} - 241^\circ$  in  $\text{CHCl}_3$  (cf. Ando, A., 1940, II, 43), converted by  $\text{Ac}_2\text{O}$  at 165—170° into  $\Delta^{11}$ -dehydroneoergosteryl acetate (I),  $\text{C}_{29}\text{H}_{40}\text{O}_2$ , m.p. 199°,  $[\alpha]_D^{19} + 41^\circ$  in  $\text{CHCl}_3$ . Hydrogenation ( $\text{Pt}\text{--black}$ ;  $\text{AcOH}\text{--Et}_2\text{O}$ ) of (I) yields dihydroneoergosteryl acetate, new m.p. 122°.

A. T. P.

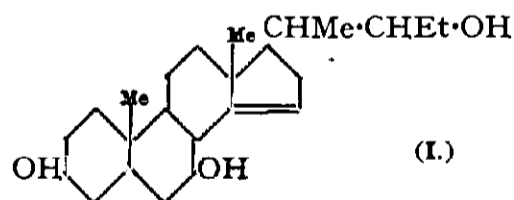
**Subsidiary sterols of yeast. VII. Zymosterol.** H. Wieland, F. Rath, and W. Benend. **VIII. Constitution of ascosterol, faecosterol, episterol, and neosterol.** H. Wieland, F. Rath, and H. Hesse (*Annalen*, 1941, 548, 19—33, 34—39; cf. A., 1929, 1200; 1937, II, 416; 1942, II, 58).—VII. Zymosterol (I),  $[\alpha]_D + 49^\circ$ , contains an easily reducible terminal  $\text{C}\cdot\text{CMe}_2$  and a non-reducible  $\text{C}\cdot\text{C}$  at  $\text{C}_{(10)}\text{--C}_{(11)}$  (cf. Heath-Brown et al., A., 1941, II, 41). Hydrogenation ( $\text{PtO}_2$ ) of the benzoate (II), m.p. 126—128° (clear at 138°),  $[\alpha]_D + 37^\circ$ , in EtOAc gives dihydrozymosteryl [ $\alpha$ -zymostenyl] benzoate (III), m.p. 140—142° (clear at 165°),  $[\alpha]_D + 41^\circ$ , and thence ( $\text{KOH}\text{--MeOH}$ )  $\alpha$ -zymostenol (IV), m.p. 128—129°,  $[\alpha]_D + 50^\circ$ , also obtained by hydrogenating (I) in EtOAc; that of zymosteryl acetate (V), m.p. 106—108°,  $[\alpha]_D + 34^\circ$ , yields  $\alpha$ -zymostenyl acetate, m.p. 128—129°,  $[\alpha]_D + 31.5^\circ$ , also obtained from (IV) by  $\text{Ac}_2\text{O}$ . Passing  $\text{HCl}$  into (III) in  $\text{CHCl}_3$  yields  $\beta$ -cholestenyl benzoate (VI), m.p. 172—174° (lit. 168°),  $[\alpha]_D + 31^\circ$  (lit. 32.5°) [and thence  $\beta$ -cholestenol (VII), m.p. 131—133° (lit. 130°) (*acetate*, m.p. 90—92°,  $[\alpha]_D + 22.8^\circ$ )].

and cholesterol (as benzoate; fully identified). Similar treatment of  $\alpha$ -cholestenyl benzoate (VIII) yields only (VI). 1 H<sub>2</sub> is absorbed by (VII) to yield cholestanol and by cholesteryl acetate to yield cholestanyl [zymostanyl] acetate. Short hydrogenation (PtO<sub>2</sub>) of (II) in Ac<sub>2</sub>O-Et<sub>2</sub>O gives (III), but during longer shaking isomerisation to (VIII) occurs; similarly  $\alpha$ -cholestenyl acetate is obtained from (V); the isomerisations are confirmed by shaking preformed (III) and (IV) with H<sub>2</sub>-Pt-AcOH, but (I) is unaffected. With Al(OPr<sup>*i*</sup>)<sub>3</sub>-cyclohexanone-PhMe or, less well, Al(OPr<sup>*i*</sup>)<sub>3</sub>-COMe<sub>2</sub>-C<sub>6</sub>H<sub>5</sub> or CuO at 300°, (I) gives zymostadienone, m.p. 104–105°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +75.5° [purified by way of the semicarbazone, m.p. 230° (decomp.)]. Similarly, (IV) gives zymostenone, m.p. 124–125°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +71.5° (70.5°) [purified by way of the semicarbazone, m.p. 243° (decomp.)], reduced by Al(OPr<sup>*i*</sup>)<sub>3</sub>-Pr<sup>*i*</sup>OH-PhMe to (IV) and a substance, m.p. 155–156°, [ $\alpha$ ]<sub>D</sub> +49°. Ozonisation of (I), but not of (IV), gives COMe<sub>2</sub>.

VIII. Ascosterol, new m.p. 140–142°, [ $\alpha$ ]<sub>D</sub> +45°, is C<sub>28</sub>H<sub>48</sub>·OH. It contains a CH<sub>2</sub>: in the side-chain and an ethylenic linking at C<sub>(7)</sub> or C<sub>(8)</sub>-C<sub>(9)</sub>. The benzoate, new m.p. 128–130°, [ $\alpha$ ]<sub>D</sub> +37.8°, with H<sub>2</sub>-PtO<sub>2</sub> in AcOH gives  $\alpha$ -ergostenyl benzoate (IX), m.p. 136–138° (lit. 118–120°) (identified by mixed m.p., hydrolysis, and then oxidation), and with Pt-N<sub>2</sub>-EtOAc gives fæcosterol benzoate (X), m.p. 144–146°, [ $\alpha$ ]<sub>D</sub> +34°. The derived fæcosterol, new m.p. 160–162°, [ $\alpha$ ]<sub>D</sub> +42° (acetate, m.p. 159–161°, [ $\alpha$ ]<sub>D</sub> +20°), has a CH<sub>2</sub>: in the same position in the side-chain but a C<sub>(8:14)</sub>-ethylenic linking; it is hydrogenated in AcOH to  $\alpha$ -ergosterol (XI) [(X) similarly yields (IX)], but is unaffected by Na-PrOH; with O<sub>3</sub> in AcOH it gives 30% of CH<sub>2</sub>O. Pt-N<sub>2</sub>-Et<sub>2</sub>O does not isomerise (X). Episterol, m.p. 150–151°, [ $\alpha$ ]<sub>D</sub> -5° (acetate, m.p. 160–162°, [ $\alpha$ ]<sub>D</sub> -3.5°), contains CH<sub>2</sub>: in the side-chain and a C<sub>(8:14)</sub>-ethylenic linking; it is reduced (H<sub>2</sub>-PtO<sub>2</sub>; AcOH) to (XI), is unaffected by Pt-N<sub>2</sub>-EtOAc, and with O<sub>3</sub> gives 45% of CH<sub>2</sub>O. Contrary to Callow (A., 1931, 618), neosterol, [ $\alpha$ ]<sub>D</sub> -42° (acetate, [ $\alpha$ ]<sub>D</sub> -66.7°), is a C<sub>(14)</sub>-epimeride of isoergosterol; with O<sub>3</sub> in AcOH it gives CHMePr<sup>*i*</sup>-CHO (44%); hydrogenation gives  $\alpha$ -dihydroergosterol (XII), but that of the benzoate, new m.p. 171–173°, [ $\alpha$ ]<sub>D</sub> -42°, or of the benzoate of (XII) gives (IX). Isolation of the above-named sterols and of (XII) from crude yeast-sterols is improved. [ $\alpha$ ] are in CHCl<sub>3</sub>.

R. S. C.

**Tetrahydroxycholane [sulphate], trihydroxycholene, and trihydroxybisorsterocholanic acid from the bile of *Rana catesbiana*, Shaw.** Y. Kurauti and T. Kazuno (Z. physiol. Chem., 1939, 262, 53–60).—The bile is extracted with Et<sub>2</sub>O and the extract is shaken with dil. aq. Na<sub>2</sub>CO<sub>3</sub> (the residual Et<sub>2</sub>O-sol. portion is hydrolysed, thereby giving cholesterol), which removes trihydroxybisorsterocholanic acid, (?) C<sub>28</sub>H<sub>44</sub>O<sub>5</sub>, m.p. 172°, [ $\alpha$ ]<sub>D</sub><sup>12</sup> +21.58° in EtOH, which gives a violet-red Liebermann but no Hammarsten reaction. It is oxidised by CrO<sub>3</sub> in AcOH to triketobisorsterocholanic acid, m.p. 230–231° (Me ester, m.p. 150°, and its oxime, m.p. 222°). Saturation of the bile (freed from Et<sub>2</sub>O-sol. substances and mucin) with NaCl gives Na tetrahydroxycholanyl sulphate (+H<sub>2</sub>O), m.p. 178°, [ $\alpha$ ]<sub>D</sub><sup>19</sup> +8.72° in H<sub>2</sub>O, which does not decolorise KMnO<sub>4</sub> or add Br and is stable to active H. It is hydrolysed by KOH to H<sub>2</sub>SO<sub>4</sub> and trihydroxycholene (I), m.p. 177°, [ $\alpha$ ]<sub>D</sub><sup>15</sup> +34.36° in MeOH (dibromide, m.p. 180°; diacetate, m.p. 180°, and non-cryst. triacetate), which immediately decolorises KMnO<sub>4</sub>. (I) is oxidised by CrO<sub>3</sub>-AcOH to triketocholene (II), m.p. 240–242° (trioxime, decomp. 247°), which does not give the Jaffe reaction with picric acid. (I) is hydrogenated (PtO<sub>2</sub> in EtOAc) to trihydroxydihydrocholene (trihydroxycholane), m.p. 185–186°, [ $\alpha$ ]<sub>D</sub><sup>12</sup> +31.54° in EtOH, which yields triketocholane, decomp. 245°. Reduction (Clemmensen) of (II) gives a non-cryst. substance which does not solidify after treatment with H<sub>2</sub>-PtO<sub>2</sub>.



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H. W.

**Bile acids. LVII. Separation of the constituents of ox bile.** H. Wieland and W. Seibert [with M. Heki] (Z. physiol. Chem., 1939, 262, 1–19).—The hydroxycholanic acids can be separated from one another by shaking their solution in Et<sub>2</sub>O with 15% aq. HCl which removes cholic acid (I) quantitatively whereas deoxycholic (II) and anthropodeoxycholic (3:7-dihydroxycholanic) acid (III) remain almost entirely in the Et<sub>2</sub>O, from which they can be removed by 25% aq. HCl; very little lithocholic (IV) and no cholanic acid pass into the aq. acid. The separation depends largely at any rate on the basicity of the OH groups. The method is applied to the separation of ox bile into (I), (II), (III), cholesterol (V), weak acids, pigment, and fatty acids (VI). Successive treatments of (VI) with KOH and LiOH removes true (VI), leaving the "subsidiary acids" from which a small amount of (III) is extracted by 25% aq. HCl; the residual material is esterified (CH<sub>2</sub>N<sub>2</sub>) and the esters are fractionally hydrolysed, whereby a small proportion of (IV) is readily removed; more drastic hydrolysis of the residual esters leads to (V) (small amount), sapocholic (VII), ursolic, and oleanolic acid. (VII) is with difficulty freed from solvent of crystallisation but appears to be C<sub>30</sub>H<sub>48</sub>O<sub>3</sub>; it is best purified through its acetate, m.p. 231–233° (Me ester, m.p. 185–186°).

H. W.

**Bile acids. LVIII. Behaviour of the diketohydroxyamic acid, C<sub>24</sub>H<sub>35</sub>O<sub>8</sub>N, and other hydroxyamic acids towards alkaline permanganate solution.** M. Schenck (Z. physiol. Chem., 1939, 262, 47–52).—Oxidation of the acids A (R = O or N·OH) by alkaline permanganate give cilianic acid and N<sub>2</sub> with a small proportion of N<sub>2</sub>O. Similar treatment of benz- and acet-hydroxyamic acid yields N<sub>2</sub>O with a small proportion of N<sub>2</sub>. The reaction appears characteristic of hydroxyamic acids. The difference in the proportions of the gases evolved is attributed to differing ease of oxidation of the resultant acids.

H. W.

**Bile acids and related substances. XXVI. Derivatives of ætiocholanic acid with oxygen in 3- and 11-position.** A. Lardon and T. Reichstein (Helv. Chim. Acta, 1943, 26, 705–715).—Me 3-keto- $\Delta^{11}$ -ætiocholenate and NHAcBr in aq. COMe<sub>2</sub> at 18° give Me 12-bromo-11-hydroxy-3-ketoætiocholenate (I), m.p. 188–190°, and amorphous material (II). CrO<sub>3</sub> in AcOH at 18° oxidises (I) to Me 12-bromo-3:11-diketoætiocholenate, m.p. 170–173°, debrominated (Zn dust and AcOH) to Me 3:11-diketoætiocholenate (III), m.p. 184–186°, [ $\alpha$ ]<sub>D</sub><sup>18</sup> +92.8° ± 2° in COMe<sub>2</sub>. Oxidation followed by debromination of (II) gives (III), Me 3:12-diketo- $\Delta^9$ -ætiocholenate, m.p. 174–176°, [ $\alpha$ ]<sub>D</sub><sup>14</sup> +91.1° ± 2° in COMe<sub>2</sub>, and non-cryst. material. Br in AcOH converts (III) into the 4-Br-ester, which passes in boiling C<sub>5</sub>H<sub>5</sub>N into Me 3:11-diketo- $\Delta^4$ -ætiocholenate, m.p. 173–177°. Me 3(a)-acetoxy- $\Delta^{11}$ -ætiocholenate and NHAcBr in aq. COMe<sub>2</sub> at 18° afford the bromohydrin (IV), m.p. 216–220°, transformed by oxidation followed by debromination into Me 11-keto-3(a)-acetoxyætiocholenate (V), m.p. 147–149°, [ $\alpha$ ]<sub>D</sub><sup>17</sup> +98.1° ± 2° in COMe<sub>2</sub>; similar treatment of the mother-liquors from (IV) affords (V) and (?) Me 12-keto-3(a)-acetoxy- $\Delta^9$ -ætiocholenate, m.p. 156–158°. Hydrolysis of (V) gives the 3(a)-OH-ester, m.p. 155–158°, oxidised to (III). Reduction (H<sub>2</sub>-PtO<sub>2</sub> in AcOH) of (III) leads to Me 3(a)- [identified by conversion into (V)] and 3(β)-hydroxy-11-ketoætiocholenate, m.p. 172–175°, [ $\alpha$ ]<sub>D</sub><sup>26</sup> +72.1° ± 2° in COMe<sub>2</sub> (acetate, m.p. 129–131°, [ $\alpha$ ]<sub>D</sub><sup>26</sup> +71.8° ± 2° in COMe<sub>2</sub>). M.p. are corr. (block).

H. W.

**Rearrangement reactions of brominated derivatives of cholesterol. VII. Preparation of  $\Delta^{1:2:4:5}$ -androstadien-17-ol-3-one.** H. H. Inhoffen, G. Zühlsdorff, and H. Minlon (Ber., 1940, 73, [B], 451–457).—2-Bromocholestanone (I) and boiling 2:6-dimethylpyridine very smoothly yield a cholestanonyl-2:6-dimethylpyridinium hydrobromide, m.p. 299–300°, whereas under similar conditions 2:4-dimethylpyridine gives  $\Delta^{1:2}$ -cholestenone. The formation of pyridinium compounds from (I) or 2:4-dibromocholestanone appears to be inhibited by Me at C<sub>(4)</sub> of the C<sub>5</sub>H<sub>5</sub>N. Androstanolone acetate is converted by Br in AcOH at room temp. into 2:4-dibromoandrostan-17-ol-3-one-acetate, m.p. 194° (decomp.), converted by boiling anhyd. C<sub>5</sub>H<sub>5</sub>N into a pyridinium hydrobromide C<sub>28</sub>H<sub>34</sub>O<sub>3</sub>NBr, m.p. 228–229°, but by boiling collidine into  $\Delta^{1:2:4:5}$ -androstadien-17-ol-3-one acetate (I), m.p. 151–152°, [ $\alpha$ ]<sub>D</sub><sup>22</sup> +28.1° in CHCl<sub>3</sub> (semicarbazone, m.p. 205–206°), in 69% yield. (I) is hydrolysed by boiling KOH-MeOH to  $\Delta^{1:2:4:5}$ -androstadien-17-ol-3-one, m.p. 168–169°, [ $\alpha$ ]<sub>D</sub><sup>23</sup> +22.5° in CHCl<sub>3</sub>, which is converted by the requisite anhydride and C<sub>5</sub>H<sub>5</sub>N into the propionate, m.p. 138–139°, butyrate, m.p. 82–83°, valerate, m.p. 76–77°, and benzoate, m.p. 215–216°. (I) is oxidised [Al(OPr<sup>*i*</sup>)<sub>3</sub> and cyclohexanone in boiling PhMe] to  $\Delta^{1:2:4:5}$ -androstadiene-3:17-dione, m.p. 139–140°, [ $\alpha$ ]<sub>D</sub><sup>24</sup> +115.8° in CHCl<sub>3</sub> (disemicarbazone, decomp. >350°, becomes discoloured at ~320°).

H. W.

**Isomerisation of 17-hydroxy-20-ketosteroids. III.** C. W. Shoppee and D. A. Prins (Helv. Chim. Acta, 1943, 26, 1004–1016).—3(β):17(a)-Diacetoxy- $\Delta^5$ -pregnen-20-one is scarcely affected when distilled with or without Zn at 210–240°/10 mm. or subjected to protracted treatment in PhMe at 110° or xylene at 140°. With C<sub>5</sub>H<sub>5</sub>N-HCO·NH<sub>2</sub> it gives a very small proportion of the 17-monoacetate. The corresponding 17(a)-benzoyloxy-3(β)-acetoxy-compound at 250–280°/10 mm. yields 3(β)-acetoxy- $\Delta^5:16$ -pregnadien-20-one (I), m.p. 174°, [ $\alpha$ ]<sub>D</sub><sup>12</sup> -29.1° ± 4° in COMe<sub>2</sub>, in 20% yield, with a small amount of pregnatrien-20-one, m.p. 142–143°, softens at ~138°, [ $\alpha$ ]<sub>D</sub><sup>13</sup> -106° ± 3° in COMe<sub>2</sub>, hydrogenated (PtO<sub>2</sub> in AcOH) to allopregnan-20-one, m.p. 128–130° (2:4-dinitrophenylhydraz-one, m.p. 222–224°), also obtained from allopregnane-3:20-dione. 17-OAc or -OBz is therefore difficultly removable from 20-ketosteroids and the direct removal of OH from this class of compounds would appear scarcely practicable. Hence it is probable that the conversion of 17(a)-hydroxy-3(β)-acetoxy- $\Delta^5$ -pregnen-20-one (II) into (I) by POCl<sub>3</sub> in C<sub>5</sub>H<sub>5</sub>N at 100° occurs through the 17-Cl-compound. (I) is also obtained in poor yield by converting (C<sub>5</sub>H<sub>5</sub>N-POCl<sub>3</sub>) 17(a)-hydroxy-3(β)-acetoxy- $\Delta^5$ -pregnen- $\Delta^{20}$ -inene into 3(β)-acetoxy- $\Delta^5:16$ -pregnadien- $\Delta^{20}$ -inene, m.p. 175–177°, [ $\alpha$ ]<sub>D</sub><sup>15</sup> -59.9° ± 3° in dioxan, which is then treated with HgO-Ac<sub>2</sub>O-AcOH followed by BF<sub>3</sub>-Et<sub>2</sub>O or with HgCl<sub>2</sub>-NH<sub>2</sub>Ph-H<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> at 60°. The product of the reaction of PBr<sub>3</sub> and C<sub>5</sub>H<sub>5</sub>N on (II) according to Juvala (A., 1930, 1401) is not homogeneous and consists largely of 17a(β)-hydroxy-3(β)-acetoxy-17a-methyl-D-homo- $\Delta^5$ -androst-17-one, m.p. 168–170° (alters at 152°); in an excess of cold C<sub>5</sub>H<sub>5</sub>N, OH is not

exchanged for Br. The mechanism of the changes is discussed. M.p. are corr. (block). H. W.

**Constituents of the adrenal cortex and related substances. LX.**  
 **$\Delta^{11}$ -Dehydropregesterone.** P. Hegner and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 715—721).—12( $\beta$ )-Hydroxyprogesterone (prep. starting from Me deoxycholate described) is converted by BzCl in  $C_6H_5N$ - $C_6H_6$  at 20° and then 60° into the benzoate, m.p. 164—166°,  $[\alpha]_D^{25} +96.2^\circ \pm 2^\circ$  in  $COMe_2$ . This passes at 310—320°/12 mm. into  $\Delta^{11}$ -dehydropregesterone, m.p. 175—177°,  $[\alpha]_D^{25} +180.5^\circ \pm 2^\circ$  in  $COMe_2$ , which in the Clauberg test has at least half the physiological activity of progesterone. The " $\Delta^{11}$ -dehydropregesterone" of Shoppee and Reichstein (A., 1941, II, 259) is probably the  $\Delta^9$ -compound. *Me nordeoxycholate 12-monoacetate* has m.p. 176—177°. M.p. are corr. (block). H. W.

**Constituents of the adrenal cortex and related substances. LXI.**  
**11-Ketoprogesterone.** P. Hegner and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 721—729).—Pregnan-12( $\beta$ )-ol-3:20-dione and BzCl in  $C_6H_6$ - $C_6H_5N$  at room temp. and then at 60° give the benzoate, m.p. 166—167°,  $[\alpha]_D^{25} +92.6^\circ \pm 1.0^\circ$  in  $COMe_2$ , which passes at 308—310°/12 mm. into BzOH and  $\Delta^{11}$ -pregnene-3:20-dione (I), m.p. 132—133°,  $[\alpha]_D^{18} +84.7^\circ \pm 3^\circ$ ,  $[\alpha]_{461}^{18} +104^\circ \pm 3^\circ$  in  $COMe_2$ . (I) with NHAcBr in aq.  $COMe_2$  at 20° gives 12-bromopregnan-11-ol-3:20-dione (II), m.p. ~238—245° (decomp.), oxidised by  $CrO_3$  in  $AcOH$ - $CHCl_3$  to 12-bromopregnane-3:11:20-trione, m.p. 176—184°, which is debrominated by Zn dust and  $AcOH$  to pregnane-3:11:20-trione (III), m.p. 154—156°,  $[\alpha]_D^{20} +119.5^\circ \pm 2^\circ$  in  $COMe_2$ . This is converted by Br in  $HBr$ - $AcOH$  into the 4-Br-compound, m.p. 158—160°, debrominated to 11-ketoprogesterone, m.p. 173—175°,  $[\alpha]_D^{18} +243.5^\circ \pm 6^\circ$ ,  $[\alpha]_{461}^{18} +283^\circ \pm 6^\circ$  in  $COMe_2$ , identical with the product from corticosterone. Oxidation of the by-products from (II) followed by debromination leads to (I), (III), probably  $\Delta^9$ -pregnene-3:11:20-trione, m.p. 184—186°, and an unidentified substance. M.p. are corr. (block). H. W.

**Constituents of the adrenal cortex and related substances. LXII.**  
**Partial synthesis of 11-dehydrocorticosterone.** A. Lardon and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 747—755).—11-Keto-3( $\beta$ )-acetoxy $\Delta^1$ -cholanic acid, m.p. 173—176° after sublimation in a high vac., or m.p. 112° and 173—176° after resolidification if cryst. from  $Et_2O$ -light petroleum (Me ester, m.p. 129—131°), is converted by successive treatments with  $SOCl_2$  and  $CH_2N_2$  in  $C_6H_6$  into 21-diazopregnan-3( $\beta$ )-ol-11:20-dione acetate, hydrolysed by  $KOH$ - $MeOH$  at 20° to the resinous alcohol; this is converted by anhyd.  $AcOH$  at 95—100° into pregnane-3( $\beta$ ):21-diol-11:20-dione 21-monoacetate (I), m.p. 178—181°, which with  $Ac_2O$ - $C_6H_5N$  affords the 3( $\beta$ ):21-diacetate, m.p. 169—171°. (I) is oxidised by  $CrO_3$  in  $AcOH$  to pregnan-21-ol-3:11:20-trione acetate, m.p. 153—155°,  $[\alpha]_D^{22} +107.2^\circ \pm 4^\circ$  in  $COMe_2$ . This with Br in  $AcOH$  affords its 4-Br-derivative, converted by boiling  $C_6H_5N$  into  $\Delta^4$ -pregnen-21-ol-3:11:20-trione acetate (dehydrocorticosterone acetate), m.p. 175—178°,  $[\alpha]_D^{22} +210.7^\circ \pm 3^\circ$  in  $COMe_2$ . M.p. are corr. (block); limit of error  $\pm 2^\circ$ . H. W.

## V.—TERPENES AND TRITERPENOID SAPOGENINS.

**Dependence of optical rotatory power on chemical constitution. XXII.** Rotatory dispersion of enantiomeric *o*-, *m*-, and *p*-nitro- and *p*-dimethylamino-benzylideneaminomethylenecamphor. B. K. Singh and S. C. Sen (*Proc. Indian Acad. Sci.*, 1943, **17**, A, 33—40).—Aminomethylene-*d*-, *-l*-, or *-dl*-camphor (A) with *o*- or *m*- $NO_2$ - $C_6H_4$ -CHO in  $MeOH$  at 45—50° gives *d*- and *l*-*o*-, m.p. 168—170°, *dl*-*o*-, m.p. 182—183°, *d*- and *l*-*m*-, m.p. 159—161°, and *dl*-*m*-nitrobenzylideneaminomethylenecamphor, m.p. 150—152°. *p*- $NO_2$ - $C_6H_4$ -CHO, (A), and  $Na_2SO_4$  in  $MeOH$  at 45—50° or, for *p*- $NMe_2$ - $C_6H_4$ -CHO, at room temp. gives *d*- or *l*-*p*-nitro-, m.p. 200—202°, *dl*-*p*-nitro-, m.p. 214—216°, *d*-, *l*-, or *dl*-*p*-dimethylamino-benzylideneaminomethylenecamphor, m.p. 66—68°.  $[M]$  decrease in the order  $p > m > o$  in  $MeOH$ ,  $EtOH$ ,  $CHCl_3$ , and  $C_6H_5N$  (decreasing in that order) but  $p > o > m$  in  $COMe_2$  (intermediate between  $EtOH$  and  $CHCl_3$ ) (cf. Betti, A., 1923, ii, 474). R. S. C.

**Attempted preparation of a homocamphor.**—See A., 1943, II, 264.

**Sesquiterpenes. LIX.** Oxidative degradation of the adduct of caryophyllene and maleic anhydride. L. Ruzicka, P. A. Plattner, and L. Werner (*Helv. Chim. Acta*, 1943, **26**, 966—974; cf. A., 1942, II, 370).—Ozonisation of the adduct does not give readily volatile compounds such as aldehyde and ketones and the acids, as Me esters, do not easily volatilise and do not give cryst. derivatives. Oxidation of the crude ozonisation product with  $KMnO_4$  in aq.  $Na_2CO_3$ , methylation of the product, and fractional distillation of the Me esters followed by hydrolysis leads to  $H_2C_2O_4$  as sole crystallisable compound from the more volatile fractions. The less volatile fractions are transformed into the corresponding anilides, thus leading to the recognition of *d*-trans-norcaryophyllenic (I), *d*-trans-caryophyllenic (II), and homocaryophyllenic acid (III). (I), m.p. 122—124.5°,  $[\alpha]_D^{15} +91.8^\circ$  in  $C_6H_6$ ,  $+89.0^\circ$  in  $CHCl_3$ , gives a Me ester, b.p. 100°/14 mm.,  $[\alpha]_D +48.6^\circ$  ( $l = 1$ ),  $[\alpha]_D^{20} +59.5^\circ$  in  $MeOH$ , and a dianilide, m.p. 178—179°,  $[\alpha]_D^{22} +178^\circ$  in  $CHCl_3$ . (II), m.p. 75—

77°,  $[\alpha]_D^{21} +35.3^\circ$  in  $C_6H_6$  [Me<sub>2</sub> ester, b.p. 85°/0.5 mm.,  $[\alpha]_D^{22} +44.5^\circ$  in  $MeOH$ ; dianilide (IV), m.p. 281—283°,  $[\alpha]_D^{15} +19^\circ$  in  $C_6H_5N$ ], is converted by boiling  $Ac_2O$  into the *cis*-anhydride, which, with  $H_2O$ , gives the *cis*-acid, m.p. 74—75°,  $[\alpha]_D^{20} -45.3^\circ$  in  $C_6H_6$  (Me<sub>2</sub> ester, b.p. 85°/0.5 mm.,  $[\alpha]_D^{20} -36.3^\circ$  in  $C_6H_6$ ; dianilide, m.p. 198—199°,  $[\alpha]_D^{20} -161^\circ$  in  $CHCl_3$ ). Esterification of (III) and conversion of the ester into the anilide leads to the isolation of (IV) and homocaryophyllendianilide, m.p. 183—184°,  $[\alpha]_D^{22} -71.4^\circ$  in  $CHCl_3$  (corresponding non-cryst. acid,  $[\alpha]_D^{15} +105^\circ$  in  $C_6H_6$ , and its Me<sub>2</sub> ester, b.p. 90°/0.5 mm.,  $[\alpha]_D^{15} +50^\circ$  in  $C_6H_6$ ). M.p. are corr. H. W.

**4:8-Dimethyl-6-isopropylazulene.**—See A., 1943, II, 258.

**Constitution of cafestol. IV.** A. Wettstein and K. Miescher (*Helv. Chim. Acta*, 1943, **26**, 788—800; cf. A., 1943, II, 203).—It is shown that cafestol (I) contains a furan ring with two double linkings. Oxidation of epoxynorcafestadienone (II) in  $C_6H_6$  by  $KMnO_4$ - $Na_2CO_3$  does not give well-defined products, whereas oxidation in  $COMe_2$  leads to apparently greatly degraded  $H_2O$ -sol. materials but no  $H_2C_2O_4$ .  $OsO_4$  reacts violently but in presence or absence of  $C_6H_5N$  only unchanged (II) could be isolated; the by-products do not yield homogeneous substances when oxidised further with  $HIO_4$ . Treatment of epoxynorcafestadienyl acetate (the free alcohol, m.p. 64—66°, becomes dark yellow when exposed to light and air) with  $Pb(OAc)_4$  in  $C_6H_6$  consumes 1 mol. of the reagent but gives very unstable products. Oxidation of cafestyl acetate by *o*- $CO_2H$ - $C_6H_4$ - $CO_2H$  in  $Et_2O$  and hydrogenation ( $PtO_2$  in  $AcOH$ ) of the product leads to cafestanetriolcarboxylolactone monoacetate [dihydroxycafestanolide monoacetate] (III), m.p. 244—245°, which is saturated, scarcely affected by catalytic hydrogenation, does not reduce  $Ag_2O$ - $NH_3$ , does not give a semicarbazone, contains 1 active H, and is not affected by  $Ac_2O$ - $C_6H_5N$  or  $CrO_3$ - $AcOH$  at room temp. (III) is hydrolysed by  $K_2CO_3$  in boiling aq.  $MeOH$  to dihydroxycafestanolide, m.p. 231—232°, degraded by  $HIO_4$  to ketonorcafestanolide B, m.p. 225—226° when rapidly heated, 231—232° (transformation into prisms) when slowly heated (2:4-dinitrophenylhydrazine, decomp. 310°). The reaction of (I), its derivatives, and kahweol with  $SbCl_3$  and other colour reactions are described. H. W.

**Irradiation of abietic acid with ultra-violet rays.** R. F. Brown, G. B. Bachman, and S. J. Miller (*J. Amer. Chem. Soc.*, 1943, **65**, 623—626).—Irradiation (Hg lamp) has no effect on abietic acid in  $C_6H_{14}$  or  $C_6H_6$ , but in  $EtOH$  gives di- (I) and tetra-hydroxyabietic acids, formed by virtue of  $MeCHO$  which is produced (separate experiment) by irradiation of the solvent  $EtOH$ . The acids are separated by making use of their insolubility in  $C_6H_{14}$  and pptg. (I) therefrom by  $Bu_2O$ . R. S. C.

## VI.—HETEROCYCLIC.

**Effect of reduction on the rotatory power of some furan compounds.** S. D. Willson (*Iowa State Coll. J. Sci.*, 1942, **17**, 161—162).—Reduction of *l*- $\beta$ -(2-furyl)valeric and *d*- $\beta$ -(2-furyl)hexoic acid to the tetrahydro- and finally to the  $Bu^a$  derivatives is accompanied in both cases by reversal in the signs of rotation, contrary to theory. Similarly in the reduction of *d*- $\beta$ -phenyl- $\beta$ -(2-furyl)propionic acid the sign remains unchanged. F. R. G.

**Acylation of 3-hydroxyfurans.** R. E. Lutz, C. E. McGinn, and P. S. Bailey (*J. Amer. Chem. Soc.*, 1943, **65**, 843—849).—3-Acetoxy-2:5-diphenylfuran (I) with  $MgMeI$ - $Et_2O$  gives the 3-O-MgI derivative (II), which with  $AcCl$  at the b.p. regenerates (I), with  $BzCl$  at 10° and then the b.p. gives 3-benzoyloxy-2:5-diphenylfuran (62%), m.p. 139—140° [not obtainable from  $(CHBz)_2$  by  $Bz_2O$ - $H_2SO_4$ ; with  $Ac_2O$ - $H_2SO_4$  at 25° or  $MgMeI$  and then  $AcCl$  (excess) gives (I)], cannot be methylated with  $MeI$  or  $Me_2SO_4$  but with 5%  $HCl$  and then  $CH_2N_2$ - $Et_2O$  gives a little 3-methoxy-2:5-diphenylfuran, with  $CH_2Cl$ - $OMe$ - $Et_2O$  at the b.p. gives 2:5-diphenyl-3-methoxymethylfuran, m.p. 75—75.5° (with  $Ac_2O$ - $H_2SO_4$  or  $PCl_5$  gives oils), and with  $ClCO_2Et$ - $Et_2O$  at the b.p. gives *Et* 2:5-diphenylfuran-3-carboxylate (III), m.p. 66—67° [unaffected by  $H_2SO_4$ - $AcOH$  at 25°; converted by  $MgEtI$ - $Et_2O$  and then  $AcCl$  into (I)]. With  $PCl_5$  at 25° and then  $H_2O$ , (III) yields 2-chloro-2:5-diphenyl-2:3-dihydrofuran-3-one, which with  $MgMeI$ - $Et_2O$  and then  $AcCl$  gives 2:5:2':5'-tetraphenyldi-2:3-dihydrofuran-3-on-2-yl (IV), m.p. 257—259°, also obtained from (I) by boiling  $FeCl_3$ -conc.  $HCl$ - $EtOH$  and converted into (I) by  $MgEtBr$ - $Et_2O$ , followed by  $AcCl$ , or in poor yield (owing to further reduction) by  $H_2$ - $PtO_2$ - $ZnCl_2$ - $HCl$ - $Ac_2O$ . With  $Br$ - $CCl_4$ , (IV) gives its 4:4'- $Br_2$ -derivative, m.p. 278—280° (decomp.), also obtained by boiling 2-chloro-4-bromo-2:5-diphenyl-2:3-dihydrofuran-3-one with  $Cu$ -bronze in  $C_6H_6$ . 3-Acetoxy-2:4:5-triphenylfuran (V) (prep. from  $CPhBz:CHBz$  by  $H_2SO_4$ - $Ac_2O$  at room temp.) with  $MgEtBr$ - $Et_2O$ - $N_2$  and then (a) 5%  $H_2SO_4$  gives 2:4:5:2':4':5'-hexaphenyldi-2:3-dihydrofuran-3-on-2-yl (VI), (b)  $Me_2SO_4$ - $C_6H_6$  gives oils, or (c)  $BzCl$  or  $AcCl$  gives 2-hydroxy-2:4:5-triphenyl-2:3-dihydrofuran-3-one.  $CPhBz:CHBz$ ,  $Bz_2O$ , and  $H_2SO_4$  at 50° give 3-benzoyloxy-2:4:5-triphenylfuran, m.p. 147.5—148°.  $FeCl_3$ -conc.  $HCl$ - $AcOH$ - $H_2O$  or  $I$ -conc.  $HCl$ - $AcOH$ - $H_2O$  oxidises (V) to (VI),

m.p. 272—275° (unaffected by Br), which with boiling  $\text{MgEtBr} \cdot \text{Et}_2\text{O} \cdot \text{N}_2$  and then (a)  $\text{Br} \cdot \text{MeOH}$  gives 2-methoxy-2:4:5-triphenyl-2:3-dihydrofuran-3-one or (b)  $\text{AcCl}$  gives (V), also formed by hydrogenation [cf. (IV)]. 4-Acetoxy-2:5-diphenyl-3-methylfuran (VII) with  $\text{MgEtBr} \cdot \text{Et}_2\text{O} \cdot \text{N}_2$  and then (a)  $\text{AcCl}$  regenerates (VII) and (b)  $\text{BzCl}$  gives 4-benzoyloxy-2:5-diphenyl-4-methylfuran (VIII), m.p. 129.5—130°, some difuranonyl (IX) being also obtained in both cases. Hydrolysis of the  $\text{O} \cdot \text{MgBr}$  derivative from (VII) and acylation of the crude oil obtained also gives (VII) and (IX). (IX) is not obtained from  $\text{CPhBz} \cdot \text{CPhMe}$  by  $\text{Bz}_2\text{O} \cdot \text{H}_2\text{SO}_4$ ; with  $\text{MgEtBr}$  and then  $\text{AcCl}$  it yields (VII). R. S. C.

**3-Hydroxy-2:5-dimesitylfuran and related compounds.** R. E. Lutz and C. E. McGinn (*J. Amer. Chem. Soc.*, 1943, **65**, 849—853).—3-Acetoxy-2:5-dimesitylfuran (I) (modified prep.) is hydrolysed by  $\text{H}_2\text{SO}_4$  (a little) in boiling  $\text{AcOH} \cdot \text{H}_2\text{O}$  (not at room temp.), absorbs 0.92 O in  $\text{KOH} \cdot 90\% \text{ MeOH}$  at room temp. to yield  $\text{COM} \cdot \text{C}(\text{OH}) \cdot \text{CH} \cdot \text{COM}$  ( $\text{M} = \text{mesityl}$ ) (II), and with  $\text{PCl}_5$  at 100°,  $\text{Br} \cdot \text{CHCl}_3$  or  $\text{I} \cdot \text{EtOH}$  at room temp., or boiling  $\text{AcOH} \cdot \text{HCl} \cdot \text{SnCl}_2$  gives 2:5:2':5'-tetramesityldi-2:3-dihydrofuran-3-on-2-yl (III), m.p. 184—185°. The 3-OM-gBr derivative, prep. from (I) by  $\text{MgEtBr} \cdot \text{Et}_2\text{O} \cdot \text{N}_2$ , with  $\text{AcCl}$  regenerates (I), with 10%  $\text{HCl}$  and then  $\text{O}_2 \cdot \text{MeOH}$  yields (III), with  $\text{Br} \cdot \text{Et}_2\text{O}$  at -10° gives (II) and a Br-compound, m.p. 129—129.5°, and with  $\text{BzCl}$  gives 3-benzoyloxy-2:5-dimesitylfuran, m.p. 116—116.5° [with  $\text{MgEtBr}$  and then  $\text{AcCl}$  gives (I)].  $\text{HCl} \cdot \text{MeOH}$  converts (I) into 3-methoxy-2:5-dimesitylfuran, m.p. 90—91° (cf. A., 1942, II, 316), also obtained from *cis*-8-methoxy- $\alpha$ - $\delta$ -dimesityl- $\Delta^7$ -buten- $\alpha$ -ol- $\beta$ -one by dry  $\text{HCl}$ , converted by  $\text{HNO}_3 \cdot \text{AcOH}$  at 100° into (II) and by  $\text{PCl}_5 \cdot \text{CHCl}_3$  into oils, but unaffected by  $\text{MgRX}$ , boiling  $\text{HCl} \cdot \text{AcOH}$ ,  $\text{KOH}$  or  $\text{NaOMe} \cdot \text{MeOH}$ ,  $\text{AcCl} \cdot \text{H}_2\text{SO}_4$ ,  $\text{NH}_2\text{OH}$ ,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , or  $\text{Zn} \cdot \text{AcOH}$ . Boiling 10:1:1  $\text{AcOH} \cdot \text{HCl} \cdot \text{H}_2\text{O}$  or  $\text{AcOH} \cdot \text{HCl} \cdot \text{SnCl}_2$  converts (III) into (II) and 2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{CO}_2\text{H}$ ,  $\text{MgEtBr}$  and then  $\text{RCOCl}$  gives the 3-RCO-furans, but  $\text{KOH} \cdot \text{MeOH}$  at room temp. and  $\text{NH}_2\text{OH}$  are without effect. With  $\text{Br} \cdot \text{CCl}_4$ , (III) gives 4-bromo-2-hydroxy-2:5-dimesityl-2:3-dihydrofuran-3-one, m.p. 143—144°, unaffected by boiling 2N- $\text{NaOMe} \cdot \text{MeOH}$ ,  $\text{PCl}_5$  at 100°,  $\text{AcCl} \cdot \text{H}_2\text{SO}_4$  at 35°,  $\text{Ac}_2\text{O} \cdot \text{H}_2\text{SO}_4$  at 100°, or  $\text{KI} \cdot \text{AcOH}$  at 80°, but converted by  $\text{AcOH} \cdot \text{H}_2\text{O} \cdot \text{HCl}$  into  $\text{COM} \cdot \text{C}(\text{OH}) \cdot \text{CBr} \cdot \text{COM}$ , by  $\text{MgMeI}$  in (*iso*- $\text{C}_5\text{H}_{11}$ ) $_2\text{O} \cdot \text{N}_2$  at 100° into a compound,  $\text{C}_{22}\text{H}_{27}\text{O}_3\text{Br}$ , m.p. 159.5—160° (hydrolysed to a compound, m.p. 139—139.5°), and by  $\text{SnCl}_2 \cdot \text{AcOH} \cdot \text{HCl}$  into  $(\text{CH}_2 \cdot \text{COM})_2$ .  $\text{COM} \cdot \text{CH} \cdot \text{CMe} \cdot \text{COM}$  with  $\text{HBr} \cdot \text{AcOH} \cdot \text{H}_2\text{SO}_4$  at 40° gives 3-bromo-2:5-dimesityl-4-methylfuran, m.p. 159—160°.  $\text{Ac}_2\text{O} \cdot \text{H}_2\text{SO}_4$  (a little) at room temp. converts (II) into 3:4-diacetoxy- (IV), m.p. 154.5—155° [short reaction gives only the enol acetate of (II)], and  $(\text{EtCO})_2\text{O} \cdot \text{H}_2\text{SO}_4$  (a trace) at 60° gives 3:4-dipropionyl-2:5-dimesitylfuran, m.p. 72—72.5°, converted into (IV) by  $\text{MgEtI}$  and then  $\text{AcCl}$ . 2-Hydroxy-2:5-dimesityl-2:3-dihydrofuran-3-one could not be obtained. M.p. are corr. R. S. C.

**Natural  $\alpha$ -,  $\beta$ -, and  $\gamma$ -tocopherols and esters of physiological interest.** J. G. Baxter, C. D. Robeson, J. D. Taylor, and R. W. Lehman (*J. Amer. Chem. Soc.*, 1943, **65**, 918—924).—Mixed tocopherols are separated from refined cottonseed oil and wheat-germ oil by short-path distillation. The tocopherols are partly separated by chromatography and then purified as  $\alpha$ -tocopheryl *H* succinate, m.p. 76—77°,  $[\alpha]_{5461}^{25} + 4.4^\circ$  in  $\text{EtOH}$ ,  $+ 2.6^\circ$  in  $\text{C}_6\text{H}_6$  (photomicrograph; Na salt; corresponding *dl*-ester, a gel), or palmitate, m.p. 42—43° (photomicrograph; corresponding *dl*-ester, m.p. 36—38°),  $\beta$ -tocopheryl azobenzene-4-carboxylate, m.p. 70—71° (photomicrograph), and  $\gamma$ -tocopheryl palmitate, m.p. 44—45°,  $[\alpha]_{5461}^{25} + 3.4^\circ$  in  $\text{C}_6\text{H}_6$  (photomicrograph). Co-crystallisation of  $\alpha$ - and (oily)  $\gamma$ -tocopheryl *H* succinates is recorded and there is little depression of the m.p. Alkaline hydrolysis ( $\text{N}_2$ ) of the esters yields  $\alpha$ - (I),  $[\alpha]_{5461}^{25} + 0.32^\circ$  in  $\text{EtOH}$ ,  $- 3.0^\circ$  in  $\text{C}_6\text{H}_6$  (allophanate, m.p. 157—158°),  $\beta$ - (II),  $[\alpha]_{5461}^{25} + 2.9^\circ$  in  $\text{EtOH}$  (allophanate, m.p. 138—139°), and  $\gamma$ -tocopherol (III),  $[\alpha]_{5461}^{25} + 2.2^\circ$  in  $\text{EtOH}$ ,  $- 2.4^\circ$  in  $\text{C}_6\text{H}_6$ , which are purified by short-path distillation. Absorption spectra of the esters and alcohols are given. The vitamin-E activity of the  $\alpha$ - and  $\gamma$ -esters, which are non-toxic to man, parallel their tocopherol contents. In the Emmerie-Engel method of analysis, (I) is oxidised faster than (II) and this slightly faster than (III); the procedure is modified so as to retard the reaction and measure the colour when all three give the same *L* val. Under identical conditions the degrees of oxidation by  $\text{AgNO}_3$  are (I) 24, (II) 30, and (III) 91%; these differences are utilised in analysing mixtures. (I), (II), and (III) give *I* vals. (Wijs) 143, 138, and 152, respectively. R. S. C.

**Condensation of  $\alpha$ -substituted acetoacetates with phenols.** VIII. **Condensation of *C*-alkylresorcinols and ethylpyrogallol with ethyl acetosuccinate.** R. H. Shah and N. M. Shah (*J. Indian Chem. Soc.*, 1942, **19**, 489—491; cf. A., 1942, II, 268).— $\text{Et}_2$  acetosuccinate (I), 1:2:4- $\text{C}_6\text{H}_3\text{Et}(\text{OH})_2$ , and 80%  $\text{H}_2\text{SO}_4$  or  $\text{POCl}_3$  at room temp. give *Et* 7-hydroxy-4-methyl-6-ethylcoumarin-3-acetate, m.p. 184—185° (acetate, m.p. 146—147°; benzoate, m.p. 123°; *Me* ether, m.p. 93—94°), hydrolysed by 2N- $\text{NaOH}$  to the corresponding acid, m.p. 221—222° (acetate, m.p. 209°; benzoate, m.p. 160°; anilide, m.p. 257°), which could not be decarboxylated. The respective 4-alkylresorcinol affords *Et* 7-hydroxy-4-methyl-6-propyl-, m.p. 170° [acetate, m.p. 100—101°; benzoate, m.p. 115—116°; *Me* ether (II), m.p. 94—95°;

corresponding acid, m.p. 199—200° (acetate, m.p. 203°; *Me* ether, m.p. 176°, obtained during prep. of (II)], and -6-butyl-coumarin-3-acetate, m.p. 165—166° [acetate, m.p. 116—117°; benzoate, m.p. 124°; *Me* ether, m.p. 88°; free acid, m.p. 205° (*Me* ether, m.p. 160°)], and *Et* 7-hydroxy-4:6-dimethylcoumarin-3-acetate, m.p. 183—184° (acetate, m.p. 168—169°). 4-Ethylpyrogallol and (I) give *Et* 7:8-dihydroxy-4-methyl-6-ethylcoumarin-3-acetate, m.p. 150—151° [acetate, m.p. 149°; benzoate, m.p. 163°; free acid ( $\text{HCl} \cdot \text{AcOH}$ ), m.p. 275° (acetate, m.p. 153—154°)]. A. T. P.

***cis-trans*-Rearrangement of *o*-coumaric acid glucoside, glucoside of *o*-hydrocoumaric acid, and the occurrence of coumarins in the tonka bean.** H. Lutzmann (*Ber.*, 1940, **73**, [B], 632—643).—The syrupy end-product of the synthesis of tetra-acetyl- $\beta$ -*D*-glucosido-coumarinic acid (A., 1939, II, 51) and  $\text{Ac}_2\text{O} \cdot \text{C}_5\text{H}_5\text{N}$  at 0°, then at room temp., give *trans*-tetra-acetyl- $\beta$ -*D*-glucosido-*o*-coumaric acid, m.p. 186—187°,  $[\alpha]_{\text{D}}^{25} - 55.3^\circ$  in  $\text{CHCl}_3$ . Ultra-violet irradiation of Na  $\beta$ -*D*-glucosido-*o*-coumarate at 40° and  $\text{pH} \sim 6.9$ , for 6 days, effects  $\sim 86\%$  *trans-cis*-transformation;  $[\alpha]_{\text{D}}^{25}$  changes from  $-7.56^\circ$  to  $-5.64^\circ$  (pure *cis*-glucoside has  $-5.75^\circ$ ), and glucose and traces of *o*-coumaric acid (I) and coumarin (II) are detected. Numerous comparisons are made of the pure *cis*- and *trans*-compounds and the product of irradiation.  $\beta$ -*D*-Glucosidohydro-*o*-coumaric acid, m.p. 173° (sinters from 143—145°),  $[\alpha]_{\text{D}}^{25} - 56.1^\circ$  in  $\text{H}_2\text{O}$ , is prepared by hydrogenation ( $\text{Pd} \cdot \text{BaSO}_4 \cdot \text{MeOH}$ ) of the glucosido-*o*-coumaric acid. Extraction with  $\text{COMe}_2$  of ripe tonka bean gives (II) and a trace of (I). Minute traces of (II) may be detected from the green fluorescence under the quartz lamp. A. T. P.

**Anthochlor pigments.** IV. **Pigments of *Coreopsis grandiflora*.** Nutt. I. T. A. Geissman and C. D. Heaton (*J. Amer. Chem. Soc.*, 1943, **65**, 677—683; cf. A., 1942, II, 421).—The yellow petals of *C. grandiflora*, Nutt., give a red colour in alkali but contain no anthochlor pigment. Extraction with  $\text{EtOH}$  at 0° yields leptosidin (probably 5-hydroxy-6-methoxy-1-3':4'-dihydroxybenzylidenecoumaran-2-one) (I), orange-yellow, m.p. 252—254° (decomp.), leptosin (II),  $\text{C}_{22}\text{H}_{22}\text{O}_{11} \cdot 2\text{H}_2\text{O}$ , orange, m.p. 229—231° (decomp.), a flavanone (probably 8-methoxybutin) (III), pale yellow, m.p. 195—197°, and luteolin (isolated as tetra-acetate).  $\text{NaOAc} \cdot \text{Ac}_2\text{O}$  converts (II) into a hexa-acetate, m.p. 233—234°, and dil.  $\text{HCl}$  at 100° yields a reducing sugar [probably glucose (osazone)] and a residue, which by acetylation yields leptosidin triacetate (IV), m.p. 164.5—165.5° [also obtained from (I) by  $\text{NaOAc} \cdot \text{Ac}_2\text{O}$ ]. In cold, dil. alkali, (II) gives a deep purple and in conc.  $\text{H}_2\text{SO}_4$  a red colour. Thus, (II) is probably the 5-glucoside of (I).  $\text{Me}_2\text{SO}_4 \cdot \text{KOH} \cdot \text{MeOH} \cdot \text{H}_2\text{O}$  converts (IV) into leptosidin  $\text{Me}_3$  (V), m.p. 156—157° (red in conc.  $\text{H}_2\text{SO}_4$ ), and a little (?) *Me*<sub>2</sub> ether, m.p. 203—205°; (V) and a small amount of a substance, m.p. 193—194°, are obtained from (I) by an excess of  $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O} \cdot \text{MeOH}$  at 0°; these findings exclude a chalcone or flavanone structure. With 3 mols. of  $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O} \cdot \text{MeOH}$ , (I) gives a *Me*<sub>1</sub> ether, m.p. 213—214° (purple in alkali) [cf. the known 5:6-( $\text{OMe}$ )<sub>2</sub>-compound, m.p. 217°].  $\text{KMnO}_4$  in  $\text{COMe}_2$  oxidises (V) to veratric acid (VI) [proof of the 3':4'-( $\text{OH}$ )<sub>2</sub>], but  $\text{H}_2\text{O}_2 \cdot \text{KOH} \cdot \text{H}_2\text{O} \cdot \text{COMe}_2$  yields a small amount of (?) a 1:1 mixture of (VI) and a dimethoxysalicylic acid (purple  $\text{FeCl}_3$  colour). In aq.  $\text{NaOH}$  at 0°, (III) is pale red, becoming dark red if kept or warmed. In warm  $\text{NaOAc} \cdot \text{Ac}_2\text{O}$  (few min.), (III) gives its triacetate (VII), m.p. 122—123.5°, but after boiling therewith for 4 hr. gives the ( $\text{OAc}$ )<sub>4</sub>-chalcone derivative, 3:2:4:1- $\text{OMe} \cdot \text{C}_6\text{H}_2(\text{OAc})_2 \cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_3(\text{OAc})_2$  1:3:4, m.p. 106—107.5°. With  $\text{Mg}$  and  $\text{HCl}$ , (III) or (VII) gives a bluish-violet colour resembling that given by butin or its triacetate.  $\text{CH}_2\text{N}_2$  (excess) and (III) in  $\text{MeOH} \cdot \text{Et}_2\text{O}$  give (?) 7:8:3':4'-tetramethoxyflavanone, m.p. 140° (lit. 144°). (III) may exist in the petals as the chalcone. The orientations assigned depend on colour reactions and biogenetic relations; the OH assigned to  $\text{C}_{15}$  in (I) and (II) and  $\text{C}_{17}$  in (III) may be at  $\text{C}_{13}$  and  $\text{C}_{15}$ , respectively. In cold, dil. alkali, (I) gives a deep red and in conc.  $\text{H}_2\text{SO}_4$  a bright red colour; the colour given by the petals in alkali is largely due to (I). R. S. C.

**Introduction of allyl residues into aromatic compounds.**—See A., 1943, II, 261.

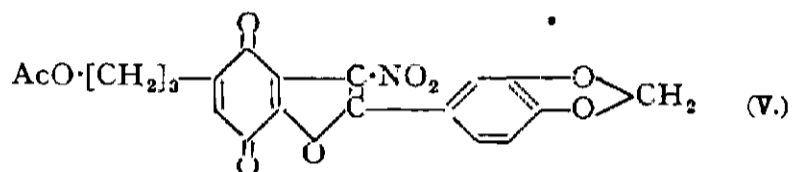
**Xanthone-2:7-dinitrile.** H. J. Fisher (*J. Amer. Chem. Soc.*, 1943, **65**, 991).—By a diazo-reaction 2:7-diamino- gives 2:7-dicyano-xanthone, cryst. R. S. C.

***Cannabis indica*.** XII. **Some analogues and a water-soluble derivative of tetrahydrocannabinol.** F. Bergel, A. L. Morrison, H. Rinderknecht, A. R. Todd, A. D. Macdonald, and G. Woolfe (*J.C.S.*, 1943, 286—287).—By condensing 4'':6''-dihydroxy-2:2:5'-trimethyl-3':4':5':6'-tetrahydrodibenzopyran with the appropriate alkyl bromide ( $\text{NaOEt} \cdot \text{EtOH}$ ) the following have been obtained: 6''-hydroxy-4''-n-hexoxy- (I), b.p. 205—209°/0.2 mm., -n-butoxy-, b.p. 185—189°/0.01 mm., -n-amyl-, b.p. 205—210°/0.1 mm., and -n-heptoxy-2:2:5'-trimethyl-3':4':5':6'-tetrahydrodibenzopyran, b.p. 210—215°/0.15 mm.; only (I) shows feeble activity by the Gayer method on rabbits. 6''-Hydroxy-2:2:5':4''-tetramethyl-3':4':5':6'-tetrahydrodibenzopyran in  $\text{C}_5\text{H}_5\text{N}$  with  $\text{POCl}_3$  gives the 6''-O-dichlorophosphoryl compound, b.p. 170°/0.15 mm., which after hydrolysis to the acid forms the  $\text{Na}_2$  phosphate. Tetrahydro-

cannabinol similarly affords the *O*-dichlorophosphoryl derivative, b.p. 185°/0.1 mm., the sol. Na<sub>2</sub> tetrahydrocannabinyl phosphate from which shows no apparent hashish activity. B.p. are bath temp. F. R. S.

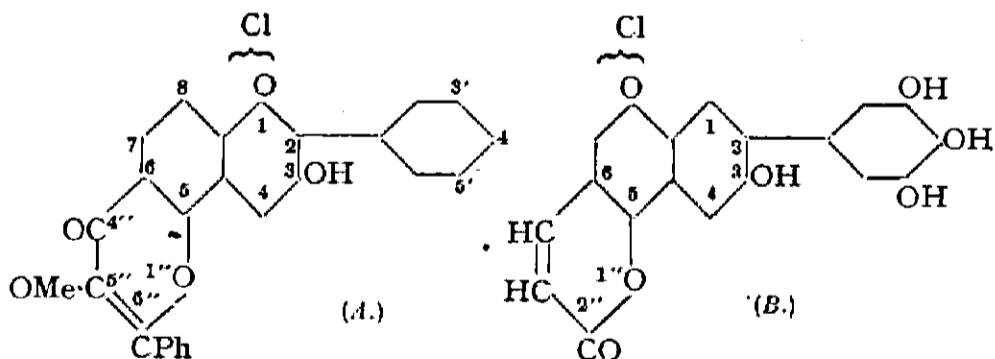
**Egonol. X. Synthesis of 2-[I]-phenylcoumarone derivatives, and their egonol reactions.** S. Kawai, T. Nakamura, and M. Yoshida. **XI. Active hydrogen atom of egonol, directly bound to carbon.** S. Kawai, N. Sugiyama, T. Nakamura, and K. Komatsu [with M. Shinkai] (*Ber.*, 1940, **73**, [B], 581—585, 586—595; cf. A., 1939, II, 383).—X. *o*-Vanillin, CHPhBr·CO<sub>2</sub>Et (I), and K<sub>2</sub>CO<sub>3</sub>·COMeEt give, after hydrolysis and decarboxylation (method: *loc. cit.*), 6-methoxy-1-phenylcoumarone, m.p. 73° (gives + e.r. = egonol reaction; cf. A., 1939, II, 32), converted by HNO<sub>3</sub> (*d* 1.38) in Ac<sub>2</sub>O into the 4-NO<sub>2</sub>-derivative, m.p. 160° (— e.r.). 2 : 4 : 1-OH·C<sub>6</sub>H<sub>3</sub>(OMe)·CHO, m.p. 41°, prepared from β-resorcaldehyde and Me<sub>2</sub>SO<sub>4</sub>·K<sub>2</sub>CO<sub>3</sub>, with (I)·K<sub>2</sub>CO<sub>3</sub>·COMeEt gives Et 2-hydroxy-5-methoxy-1-phenylcoumaran-1-carboxylate, and thence 5-methoxy-1-phenylcoumarone, m.p. 83° (— e.r.)! 2 : 5 : 1-(OH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO·BzCl·K<sub>2</sub>CO<sub>3</sub>·Et<sub>2</sub>O yield 2 : 5 : 1-OH·C<sub>6</sub>H<sub>3</sub>(OBz)·CHO, m.p. 108°, which with (I) and K<sub>2</sub>CO<sub>3</sub> in COMeEt gives 2-hydroxy-1-phenylcoumarone, m.p. 185.5° (+ e.r.); 30% H<sub>2</sub>O<sub>2</sub> in AcOH at 40—45° gives an impure product (constitution discussed).

XI. Acetylegonol[6-methoxy-1-3' : 4'-methylenedioxy-4-γ-acetoxypropylcoumarone] (II) and Br·AcOH give 4-bromoacetylegonol (III), m.p. 124.5—125° (— e.r.), converted by KOAc in *iso*-C<sub>8</sub>H<sub>11</sub>·OH into 4-bromoegonol, m.p. 164—165°. (II) and HNO<sub>3</sub> (*d* 1.38)·Ac<sub>2</sub>O at —5° to —10° give 3-nitro- (IV), m.p. 160° (+ e.r.; 70—80° for 0.5 hr.), 4-nitro-, m.p. 161° (— e.r.), and some 6-nitro-acetylegonol, m.p. 139° (+ e.r.). (IV) and 30% H<sub>2</sub>O<sub>2</sub>·AcOH at 70—75° yield 3-nitronoregonolonidin acetate (V), m.p. 144—145°. (III) and 30%



H<sub>2</sub>O<sub>2</sub>·AcOH at 60—70° give a product, which with CPh·CH<sub>2</sub>Br yields phenacyl 2-bromo-6-3' : 4'-methylenedioxybenzoyloxy-5-methoxy-3-α-hydroxy-γ-acetoxypropylbenzoate, C<sub>29</sub>H<sub>25</sub>O<sub>11</sub>Br, m.p. 172—173°. The content of active H in several of these compounds is determined and theoretical aspects are discussed. A. T. P.

**Flavylium salts containing pyrone rings.** L. R. Row and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **15**, A, 118—122).—7-Hydroxy-3-methoxyflavone-8-aldehyde with the appropriate nuclear hydroxy-ω-hydroxyacetophenone in HCl·EtOH·EtOAc at 0° gives 3 : 4'-di- (numbering as A) (prep. in EtOAc) (83%), +2H<sub>2</sub>O, m.p. 227—229°, 3 : 3' : 4'-tri- (60%), +2H<sub>2</sub>O, m.p. 240—242° (decomp.), and 3 : 3' : 4' : 5'-tetra-hydroxy-5'-methoxy-6'-phenyl-1'' : 4''-pyrono-2'' : 3''-5 : 6-flavylium chloride (58%), +4H<sub>2</sub>O, m.p. >320°. Um-



belliferone-8-aldehyde gives similarly 3 : 4'-di- (65%), +0.5H<sub>2</sub>O, m.p. 255—257° (decomp.), 3 : 3' : 4'-tri- (65%), +H<sub>2</sub>O, m.p. 225—227° (decomp.), and 3 : 3' : 4' : 5'-tetra-hydroxy-1'' : 2''-pyrono-6'' : 5''-5 : 6-flavylium chloride (B) (91%), +3H<sub>2</sub>O, m.p. >320°. The salts readily lose halogen to give colour bases, have weak tinctorial properties, and fluoresce only slightly in H<sub>2</sub>SO<sub>4</sub>. R. S. C.

**Natural coumarins. LII. Constitution of oroselone.** E. Späth, N. Platzer, and H. Schmid (*Ber.*, 1940, **73**, [B], 709—718; cf. A., 1939, II, 485).—Athamantin (I), [α]<sub>D</sub><sup>25</sup> +96° in MeOH, and HCl·MeOH give Bu<sup>β</sup>CO<sub>2</sub>H and oroselone (II), C<sub>14</sub>H<sub>10</sub>O<sub>3</sub>, sublimes at 140—150°/0.1 mm., m.p. 188—189°, [α]<sub>D</sub><sup>20</sup> 0°; (II) is most probably 5'-(α-methylvinyl)furan-2' : 3'-7 : 8-coumarin, and with Me<sub>2</sub>SO<sub>4</sub>·aq. NaOH gives the *Me* ether, C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>, m.p. 233°, of orosolonic acid. Hydrogenation (Pd·C; AcOH) of (II) at 18° yields dihydro- (III), m.p. 142°, and tetrahydro- (IV), m.p. 60—62°, and at 40—50° hexahydro-oroselone (V), m.p. 98°. (IV) and aq. KMnO<sub>4</sub>·NaOH give (CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub> + Pr<sup>β</sup>CO<sub>2</sub>H. (V) with CH<sub>2</sub>N<sub>2</sub> yields the *Me* ester, C<sub>15</sub>H<sub>20</sub>O<sub>4</sub>, m.p. 72—73°, of hexahydro-oroselonic acid, further methylated to its *Me* ether, C<sub>16</sub>H<sub>22</sub>O<sub>4</sub>, an oil (OH also is methylated). (V) is unchanged with Ac<sub>2</sub>O at 150—160°. (V) and HNO<sub>3</sub> (*d* 1.4) at 20°, then at 100° (bath), give (CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>. (II) and O<sub>3</sub>·CHCl<sub>3</sub> yield 2 : 4 : 1 : 3-(OH)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CHO)<sub>2</sub> and (less O<sub>3</sub>) 7-hydroxycoumarin-8-aldehyde (VI), m.p. 186.5—187°. (III) similarly gives a little

(VI) and Pr<sup>β</sup>CO<sub>2</sub>H. In (III) the CMe·CH<sub>2</sub> becomes Pr<sup>β</sup>, in (IV) the coumarin ring is also hydrogenated, and in (V) the furan ring.

A. T. P.

**Degradation of coumarones and thionaphthens by ozone.** A. von Wacek, H. O. Eppinger, and A. von Bézard (*Ber.*, 1940, **73**, [B], 521—531).—O<sub>3</sub> is quantitatively added by coumarone (I) in indifferent solvents and the ozonide is decomposed by warm H<sub>2</sub>O into *o*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (~25%), *o*-OH·C<sub>6</sub>H<sub>4</sub>·CHO (~40%), HCO<sub>2</sub>H, CO<sub>2</sub>, and *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> (~10%). *o*-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·O·CHO and *o*-CHO·C<sub>6</sub>H<sub>4</sub>·O·CO<sub>2</sub>H are presumably intermediates. Resinification is not pronounced. The solvent (EtCl, AcOH, COMe<sub>2</sub>, CHCl<sub>3</sub>) has no influence on the reaction products or their amounts. Fission of the furan ring occurs during the primary ozonisation and not by secondary oxidation by H<sub>2</sub>O<sub>2</sub> since reductive fission of the ozonide leads to *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>. It is improbable that (I) reacts in a mesomeric form since *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> is obtained from *o*-OH·C<sub>6</sub>H<sub>4</sub>·CH·CH<sub>2</sub> which has no mesomeric form whilst the possibly mesomeric C<sub>6</sub>H<sub>4</sub>>O does not add O<sub>3</sub>. *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> is obtained by secondary oxidation of *o*-OH·C<sub>6</sub>H<sub>4</sub>·CHO which has been effected by H<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>5</sub>, etc.; this change occurs to only a small extent by ozonisation of OH·C<sub>6</sub>H<sub>4</sub>·CHO but a decomp. ozonide can behave as an oxidising agent; thus, *o*-OH·C<sub>6</sub>H<sub>4</sub>·CHO is almost quantitatively converted into *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> by oleic acid ozonide. 1-Methylcoumarone behaves similarly but gives AcOH in place of HCO<sub>2</sub>H. *o*-OAc·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and *o*-OAc·C<sub>6</sub>H<sub>4</sub>·CHO could not be isolated; the possibility that the peroxidic compound of the decomp. ozonide accelerates their hydrolysis is strengthened by the observation that the first compound is hydrolysed by NaHCO<sub>3</sub> only after addition of H<sub>2</sub>O<sub>2</sub>. 2-Methylcoumarones give only *o*-OH·C<sub>6</sub>H<sub>4</sub>·COMe with *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, which can be obtained from it by oxidation with H<sub>2</sub>O<sub>2</sub>. Coumarones methylated in the C<sub>6</sub>H<sub>6</sub> nucleus afford the corresponding *o*-hydroxytoluic acids and aldehydes with the methylpyrocatechols. In principle thionaphthen behaves similarly to (I) but the instability of thiols towards oxidising agents involves their isolation as the corresponding disulphides. Small quantities of sulphonic acids are also obtained; these could not be certainly identified on account of their small yield but appear to be phenol-*o*-sulphonic acids. The yields of (S·C<sub>6</sub>H<sub>4</sub>·OH-*o*)<sub>2</sub> and (S·C<sub>6</sub>H<sub>4</sub>·CHO-*o*)<sub>2</sub> attain 50% and 20% respectively. The ozonisation of coumarones is a simple quant. degradation which gives very small amounts of resin. The products are easily obtained pure. The secondary peroxidic action can cause rupture of the C chains which are replaced by OH groups. H. W.

**Photo-oxidation of thioketones.**—See A., 1943, II, 265.

**Pyrrolidines and piperidines.**—See B., 1943, II, 174.

**Isomerisation during dehydrogenations in the pyridine series.** II. V. Prelog and E. Moor [with J. Führer] (*Helv. Chim. Acta*, 1943, **26**, 846—848).—3-Acetyl-1-methylpiperidine (I) is converted by Se at 300° into 2 : 3-dimethylpyridine, isolated as the picrate, m.p. 183—184°, platinichloride, m.p. 196°, and aurichloride, m.p. 164°. (I) is reduced by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O and NaOMe in MeOH at 170—180° to 1-methyl-3-ethylpiperidine, which is largely unchanged by Se at 300° but passes at 350° into 3-ethylpyridine. H. W.

**New synthesis of 2-aminopyridine derivatives.** A. Dornow and P. Karlson (*Ber.*, 1940, **73**, [B], 542—546).—OEt·C(NH)·CH<sub>2</sub>·CO<sub>2</sub>Et (I) condenses with (CO)<sub>2</sub>-compounds (mol. ratio, 2 : 1) to amidine-like intermediates COR'·CH<sub>2</sub>·CH·C(CO<sub>2</sub>Et)·C(NH)·N·C(OEt)·CH<sub>2</sub>·CO<sub>2</sub>Et (II), which then undergo ring-closure with hydrolytic elimination of CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> and production of 2-aminopyridine derivatives. (II) and OEt·CH·CH·CH(OEt)<sub>2</sub> at 100° slowly afford *Et* 2-aminopyridine-3-carboxylate, b.p. 133°/12 mm., m.p. 92° (picrate, m.p. 199°). This is hydrolysed by boiling conc. HCl to the acid, m.p. 308° (decomp.) (hydrochloride, m.p. 214—216°; picrate, m.p. 229—230°), which passes above its m.p. into 2-aminopyridine (picrate, m.p. 218°) and is converted by HNO<sub>2</sub> into 2-hydroxypyridine-3-carboxylic acid, m.p. 255° (decomp.). (I) and OEt·CMe·CH·CH(OEt)<sub>2</sub> or CH<sub>2</sub>Ac·CHO yield *Et* 2-amino-6-methylpyridine-3-carboxylate, b.p. 134°/12 mm., 140°/15 mm., m.p. 84° (picrate, m.p. 185—186°), hydrolysed to the acid, m.p. 298° (decomp.), identified by conversion into the corresponding OH-acid, m.p. 227° (decomp.). Similarly CH<sub>2</sub>Ac<sub>2</sub> affords *Et* 2-amino-4 : 6-dimethylpyridine-3-carboxylate, m.p. 110° (picrate, m.p. 163°), which gives the acid, m.p. 258° (decomp.) (picrate, m.p. 227—228°). OBz·CH<sub>2</sub>·CHO transforms (I) into the amidine [(II) (R = Ph)], m.p. 117—118°, converted by warm EtOH into CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> and *Et* 2-amino-6-phenylpyridine-3-carboxylate, m.p. 108° (picrate, m.p. 201—202°). H. W.

**Preparation of 2-*p*-aminobenzenesulphonamidopyridine.** C. W. Shen and H. N. Chen (*J. Chinese Chem. Soc.*, 1941, **8**, 4—6).—*p*-NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Cl and 2-C<sub>6</sub>H<sub>4</sub>N·NH<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> yield 84% of 2-*p*-acetamido-, hydrolysed (~100%) to 2-*p*-amino-benzenesulphonamidopyridine. A. Li.

**Synthesis of vitamin-B<sub>6</sub>.** J. H. Mowat, F. J. Pilgrim, and G. H. Carlson (*J. Amer. Chem. Soc.*, 1943, **65**, 954—955).—5-Cyano-2-methyl-6-pyridone-4-carboxylamide (prep. from the Et ester by NH<sub>3</sub>-

MeOH at 0°), m.p. >300° (decomp.), with POCl<sub>3</sub> at 145—150° gives 4:5-dicyano-2-methyl-6-pyridone, m.p. 241—243°, converted by fuming HNO<sub>3</sub> and a little CO(NH<sub>2</sub>)<sub>2</sub> in Ac<sub>2</sub>O into the 3-NO<sub>2</sub>-derivative, m.p. 242—244°, which with PCl<sub>3</sub> in PhCl at 135° yields 6-chloro-3-nitro-4:5-dicyano-2-methylpyridine, m.p. 86—86.5°. H<sub>2</sub>-PtO<sub>2</sub> in Ac<sub>2</sub>O then gives 6-chloro-3-amino-4:5-dicyano-2-methylpyridine, m.p. 221—221.5°, which with H<sub>2</sub>-PdCl<sub>2</sub>-HCl-MeOH-H<sub>2</sub>O at 30° yields 3-amino-2-methyl-4:5-di(aminomethyl)pyridine tri-chloride (the sulphate, B, 2H<sub>2</sub>SO<sub>4</sub>, is obtained in H<sub>2</sub>SO<sub>4</sub>-MeOH-H<sub>2</sub>O), converted by HNO<sub>2</sub> into vitamin-B<sub>6</sub> hydrochloride. R. S. C.

**Pyridine derivatives.**—See B., 1943, II, 245.

**Use of <sup>15</sup>N as a tracer element in chemical reactions. Mechanism of the Fischer indole synthesis.** C. F. H. Allen and C. V. Wilson (*J. Amer. Chem. Soc.*, 1943, 65, 611—612).—<sup>15</sup>NH<sub>3</sub> (see below) is converted into, successively, <sup>15</sup>NH<sub>2</sub>Bz, <sup>15</sup>NH<sub>2</sub>Ph, <sup>15</sup>NHPh·NH<sub>2</sub> (I), <sup>15</sup>NHPh·N:CPhMe, and 2-phenylindole (II). The % of the total N present as <sup>15</sup>N in <sup>15</sup>NH<sub>3</sub>, (I), and (II) was 7.28, 3.92±0.3, and 7.06±0.06, respectively, thus proving that the \*N is eliminated. Formation of o-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CPh:NH precedes, but removal of the NH as NH<sub>3</sub> may precede or follow, ring-closure. R. S. C.

**Polynuclear condensed systems with heterocyclic rings. XI. Attempted ring-closure of 2:3-phenyl-pyrrole- and -indole-carboxylic acids.** W. Borsche and A. Klein (*Annalen*, 1941, 548, 64—74).—1:2:5-Triphenylpyrrole-3-carboxyl chloride (prep. by SOCl<sub>2</sub>), a resin, with NH<sub>2</sub>Ph in boiling C<sub>6</sub>H<sub>6</sub> gives the anilide, m.p. 171°, with MeOH gives the Me ester, m.p. 156—157°, and with AlCl<sub>3</sub>-C<sub>6</sub>H<sub>6</sub> at 60° gives 3-benzoyl-1:2:5-triphenylpyrrole, m.p. 238°, but internal ring-closure could not be effected. Crude CH<sub>2</sub>Ph·CO·CH(CH<sub>2</sub>Bz)·CO<sub>2</sub>Et (I) and NH<sub>3</sub> in Et<sub>2</sub>O at room temp. give Et β-amino-γ-phenyl-α-phenacylcrotonate, m.p. 166—167°, converted by boiling N-H<sub>2</sub>SO<sub>4</sub> into Et 5-phenyl-2-benzylpyrrole-3-carboxylate m.p. 137°, and thence the derived acid, m.p. 181°, the chloride of which could not be characterised or cyclised. NH<sub>2</sub>Ph and (I) in AcOH at 100° give Et 1:5-diphenyl-2-benzylpyrrole-3-carboxylate, m.p. 100—101°, and thence the acid, m.p. 191°, which could not be cyclised. NHPh·NHMe (II) and CH<sub>2</sub>Ph·CO·CO<sub>2</sub>Et in boiling HCl-MeOH-H<sub>2</sub>O give 3-phenyl-1-methylindole-2-carboxylic acid, m.p. 197—198°, which in conc. H<sub>2</sub>SO<sub>4</sub> gives 3-phenyl-1-methylindole; the derived acid chloride, m.p. 120°, b.p. 180°/0.5 mm., with AlCl<sub>3</sub>-C<sub>6</sub>H<sub>6</sub> gives 1-methyl-1'-indenono-2':3'-2:3-indole, m.p. 147—148° (2:4-dinitrophenylhydrazones, m.p. 313—314°). Ph·[CH<sub>2</sub>]<sub>2</sub>·CO·CO<sub>2</sub>Et and (II) give similarly 3-benzyl-1-methylindole-2-carboxylic acid, m.p. 194° (chloride, m.p. 117—118°), and 1-keto-9-methyl-1:4-dihydro-2:3-benzcarbazole, m.p. 215—216°. CH<sub>2</sub>Bz·CO<sub>2</sub>Et with (II) in MeOH gives the as-phenylmethylhydrazones, m.p. 128°, which with HCl-EtOH at room temp. and then the b.p. gives Et 2-phenyl-1-methylindole-3-carboxylate, m.p. 97° (picrate, m.p. 137—138°), and the acid, m.p. 201—202°, which with SOCl<sub>2</sub> and then AlCl<sub>3</sub>-C<sub>6</sub>H<sub>6</sub> gives 3-benzyl-2-phenyl-1-methylindole, m.p. 130° (2:4-dinitrophenylhydrazones, m.p. 269°), but does not undergo ring-closure. CH<sub>2</sub>Ph·C(CO<sub>2</sub>H)·N·NHPh and boiling HCl-EtOH give Et 3-phenylindole-2-carboxylate (III) and 3-phenylindole. NaOH-MeOH hydrolyses (III) to the amorphous acid (IV), m.p. 186°, the chloride, darkens at 160°, m.p. 164° (decomp.), resolidifies, remelts >360°, of which at 175—180° or with AlCl<sub>3</sub> in PhNO<sub>2</sub> at room temp. gives 3:6-diketobis-(3'-phenylindole-1':2'-)1:2:4:5-piperazine, hydrolysed by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in C<sub>6</sub>H<sub>5</sub>N at 200° to 3-phenylindole-2-carboxylhydrazide, m.p. 227° (CHPh derivative, m.p. 237°).

CH<sub>2</sub>Ph·C(CO<sub>2</sub>H)·N·NH·C<sub>6</sub>H<sub>4</sub>Me-p (prep. from p-C<sub>6</sub>H<sub>4</sub>Me·N<sub>2</sub>Cl and CH<sub>2</sub>Ph·CHAc·CO<sub>2</sub>Et in NaOH-MeOH-H<sub>2</sub>O at 0°), m.p. 145—146°, with hot HCl-EtOH gives 3-phenyl-5-methylindole, m.p. 105°, and its 2-carboxylic acid, m.p. 219—220°; the derived chloride, m.p. 170° (decomp.), resolidifies, gives, as above, 3:6-diketobis-(3'-phenyl-5'-methylindole-1':2'-)1:2:4:5-piperazine, m.p. >360°.

R. S. C.

**Condensation reactions of cinchonin- and quinald-aldehyde.** H. Kaplan and H. G. Lindwall (*J. Amer. Chem. Soc.*, 1943, 65, 927—928).—Quinoline-2-aldehyde (I) [semicarbazone, m.p. 232—234° (decomp.)] and quinoline (II) in boiling 80% EtOH with or without NH<sub>4</sub>Et<sub>2</sub> (6 drops) give αβ-di-2-quinolylethyl alcohol, m.p. 167—168°, but in AcOH + Ac<sub>2</sub>O (few drops) at 120° or the b.p. or in Ac<sub>2</sub>O-ZnCl<sub>2</sub> (a little) at 120° gives αβ-di-2-quinolylethylene, m.p. 326°. With lepidine (III) in 80% EtOH with or without NH<sub>4</sub>Et<sub>2</sub>, (I) gives α-2-quinolyl-β-4-quinolylethyl alcohol, m.p. 191—192°. Quinoline-4-aldehyde (IV) [semicarbazone, m.p. 244—245° (decomp.)] and (II) in boiling Pr<sup>o</sup>OH with or without NH<sub>4</sub>Et<sub>2</sub> (6 drops) give α-4-quinolyl-β-2-quinolylethyl alcohol, m.p. 180—182° (benzoate, m.p. 162°). Similar condensation of (III) and (IV) could not be effected, but in AcOH containing a little Ac<sub>2</sub>O or ZnCl<sub>2</sub> at 110° they give αβ-di-4-quinolylethylene, m.p. 207°, also obtained from (III) by old SeO<sub>2</sub>. p-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH<sub>2</sub> with (I) in boiling Bu<sup>o</sup>OH-PhMe or (IV) in boiling AcOH gives N<sup>4</sup>-2-, m.p. 188—189° (decomp.), and N<sup>4</sup>-4-quinolylmethylenesulphanilamide, m.p. 151—153°, respectively. (I) is thus more reactive than (IV). R. S. C.

**Application of lithium compounds of nitrogen heterocycles to antimalarial syntheses.** S. M. Spatz (*Iowa State Coll. J. Sci.*,

1942, 17, 129—132; cf. A., 1940, II, 190; 1942, II, 114).—In the reaction between LiBu<sup>a</sup> and halogenated C<sub>5</sub>H<sub>3</sub>N and quinoline (I), addition of LiBu<sup>a</sup> may occur in absence of sufficient negative substituents, thereby reducing the yield of Li aryl. In an attempt to combine the antimalarial action of (I) and acridine compounds 6-methoxyquinoline was treated with m-C<sub>6</sub>H<sub>4</sub>LiCl, giving 6-methoxy-2-m-chlorophenylquinoline, m.p. 110—111° (picrate, m.p. 196—197°), oxidised (BzO<sub>2</sub>H in CHCl<sub>3</sub>) to its N-oxide, m.p. 153—154° (picrate, m.p. 158.5—159°), which with POCl<sub>3</sub> gives 4-chloro-6-methoxy-2-m-chlorophenylquinoline, m.p. 153—154°, which is also obtained from 4-chloro-6-methoxyquinoline and m-C<sub>6</sub>H<sub>4</sub>LiCl, and with NEt<sub>2</sub>·[CH<sub>2</sub>]<sub>3</sub>·CHMe·NH<sub>2</sub> yields 4-δ-diethylamino-α-methylbutylamino-6-methoxy-2-m-chlorophenylquinoline. Similarly prepared were 6-methoxy-2-p-chlorophenylquinoline, m.p. 194—195° (picrate, m.p. 205°; N-oxide, m.p. 166—168°; 4-Cl-derivative, m.p. 163.5—164°), 4-δ-diethylamino-α-methylbutylamino-6-methoxy-2-p-chlorophenyl-, amorphous; 6-methoxy-2-phenyl-, m.p. 132—133° (picrate, m.p. 205°; N-oxide, m.p. 170—171°; 4-Cl-derivative), and 4-δ-diethylamino-α-methylbutylamino-6-methoxy-2-phenyl-quinoline. o-C<sub>6</sub>H<sub>4</sub>Li·OMe (from o-C<sub>6</sub>H<sub>4</sub>Br·OMe) gives 2-o-anisylquinoline, b.p. 201—204°/2 mm. [hydrochloride, m.p. 184.5—185°; picrate, m.p. 177—178°; N-oxide, m.p. 178—178.5° (picrate, m.p. 133.5—134.5°); 4-Cl-derivative, m.p. 96—98° (picrate, m.p. 200—201°)], converted into 4-δ-diethylamino-α-methylbutylamino-2-o-anisylquinoline, b.p. 248—255°/0.025 mm.

F. R. G.

**Synthesis of 4:5-trimethyleneisoquinoline and derivatives of this base.** E. Späth and F. Kittel (*Ber.*, 1940, 73, [B], 478—483).—1-Aminomethyl-1:2:3:4-tetrahydronaphthalene (I) is converted into its formyl derivative, an oil, transformed by P<sub>2</sub>O<sub>5</sub> in boiling PhMe into 4:5-trimethylene-3:4-dihydroisoquinoline, m.p. 32—33° [picrate, m.p. 211—212° (vac.; decomp.)]. This is dehydrogenated (Pd-sponge at 200°) to 4:5-trimethyleneisoquinoline, m.p. 47—48° [picrate, m.p. 230—231° (vac.; decomp.)] (cf. A., 1939, II, 342). (I) is transformed into its Ac derivative, m.p. 89—90°, and thence successively into 1-methyl-4:5-trimethylene-3:4-dihydroisoquinoline, b.p. 100—120° (bath)/0.01 mm. [picrate, m.p. 221° (vac.; decomp.)], and 1-methyl-4:5-trimethyleneisoquinoline, b.p. 80—100° (bath)/0.01 mm. [picrate, m.p. 203—204° (vac.; decomp.)]. The following series are obtained similarly: 1-propionamidomethyl-1:2:3:4-tetrahydronaphthalene, b.p. 140—150° (bath)/0.01 mm., non-cryst. 1-ethyl-4:5-trimethylene-3:4-dihydroisoquinoline, b.p. 100°/0.01 mm. (picrate, m.p. 165—166°), and 1-ethyl-4:5-trimethyleneisoquinoline [picrate, m.p. 191° (vac.; decomp.)]; 1-benzamidomethyl-1:2:3:4-tetrahydronaphthalene, m.p. 127—128°, 1-phenyl-4:5-trimethylene-3:4-dihydroisoquinoline, m.p. 93—94° [picrate, m.p. 190—191° (decomp.)], and non-cryst. 1-phenyl-4:5-trimethyleneisoquinoline, b.p. 130—150° (bath)/0.01 mm. [picrate, m.p. 179—180° (vac.; decomp.)]; 1-phenylacetamidomethyl-1:2:3:4-tetrahydronaphthalene, m.p. 83—84°, non-cryst. 1-benzoyl-4:5-trimethylene-3:4-dihydroisoquinoline, b.p. 140—150° (bath)/0.01 mm. (non-cryst. picrate), and 1-benzyl-4:5-trimethyleneisoquinoline [picrate, m.p. 194—196° (vac.; decomp.)].

H. W.

**Polynuclear condensed systems with heterocyclic rings. X. Derivatives of 6:7-dihydroxyquinoline.** W. Borsche and J. Bartheimer (*Annalen*, 1941, 548, 50—63).—Prep. of quinolines from o-NH<sub>2</sub>-aldehydes, NH<sub>2</sub>Ar, and ketones is improved by using the bases NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH:NAr etc., which are prepared from NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH:NAr etc. by Na<sub>2</sub>S (cf. Rilliet, A., 1921, i, 567; 1922, i, 839). 4:5:3:1-CH<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>(NH<sub>2</sub>)·CH:N·C<sub>6</sub>H<sub>4</sub>Me-p, m.p. 144—145° (loc. cit., 134.5°), with p-OMe·C<sub>6</sub>H<sub>4</sub>·COMe and a little aq. NaOH in EtOH at the b.p. gives 6:7-methylenedioxy-2-p-anisylquinoline (~75%), m.p. 181°; use of the appropriate ketone gives similarly 6:7-methylenedioxy-2-p-chlorophenyl- (90%), m.p. 183°, -2:3-diphenyl-, m.p. 148°, and -2:3-trimethylene-quinoline (90%), m.p. 175—176° (from CH<sub>2</sub>Ac·CO<sub>2</sub>Et), 6:7-methylenedioxy-2-methylquinoline-3-carboxylic acid, m.p. 295° (evolution of CO<sub>2</sub>) [the Et ester (70%), m.p. 157—158°, is obtained by use of piperidine instead of NaOH], (from cyclohexanone) 6:7-methylenedioxy-1:2:3:4-tetrahydroacridine (75%), m.p. 137—138°, and its 3-Me derivative (80%), m.p. 190—191°, and 6:7-methylenedioxy-1':2'-dihydroindeno-1':2'-2:3-quinoline (90%), m.p. 182—183° (lit. 186°). 3:4:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO and HNO<sub>3</sub> (d 1.395) in AcOH give the 6-NO<sub>2</sub>-derivative (I) (~80%) and thence 6-nitro-veratrylidene-p-toluidine, m.p. 139°. The derived NH<sub>2</sub>-compound, m.p. 123—124° (lit. 115°), gives, as above, 6:7-dimethoxy-2-phenyl- (II), m.p. 227°, -2-p-anisyl- (80%), m.p. 180° (picrate, m.p. 256°), -2-p-chlorophenyl- (90%), m.p. 144°, and -2:3-trimethylene-quinoline (85%), m.p. 112—113°, (by use of piperidine) Et 6:7-dimethoxy-2-methylquinoline-3-carboxylate (III) (85%), m.p. 116—117°, 6:7-dimethoxy-1:2:3:4-tetrahydroacridine (IV) (80%), m.p. 124° (picrate, m.p. 247°; methiodide, m.p. 226—228°), and its 3-Me derivative (90%), m.p. 150°, and 6:7-dimethoxy-1':2'-dihydroindeno-1':2'-2:3-quinoline (75%), m.p. 197° (picrate, m.p. 266°). 3:4:6:1-CH<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)·CH:N·C<sub>6</sub>H<sub>4</sub>Me-p has m.p. 124—125° (lit. 121.5°). 6:7-Dimethoxy-2-phenylcinchonic acid [prep. from 3:4:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·NH<sub>2</sub>, PhCHO, and AcCO<sub>2</sub>H in AcOH at 100°], m.p. 255° (decomp.), gives (II) when distilled. Ph 6-nitro-3:4-dimethoxystyryl ketone (prep. by nitration as above), m.p. 185°, with Na<sub>2</sub>S-EtOH gives the NH<sub>2</sub>-ketone, m.p. 196°, without ring-closure. KOH-MeOH-H<sub>2</sub>O hydrolyses (III) to the corresponding acid, m.p. 238—

240° (decomp.), which is better obtained directly by use of NaOH and when heated at 0.1 mm. gives 3 : 6-dimethoxy-2-methylquinoline (V), b.p. 185—190°/13 mm. [picrate, m.p. 222—223° (lit. 217°)]. With 33% aq. K<sub>2</sub>CO<sub>3</sub> in COMe<sub>2</sub>, (I) gives  $\beta$ -hydroxy- $\beta$ -6-nitro-3 : 4-dimethoxyphenylethyl Me ketone, m.p. 145—146°, dehydrated in hot EtOH or AcOH to 6-nitro-3 : 4-dimethoxystyryl Me ketone, m.p. 174—175°, which with Zn-HCl-AcOH is reduced and cyclised to give (V). With *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O at 160°, (V) gives a *phthalylidene* derivative, m.p. 207—208°, and with HI-AcOH gives amorphous 6 : 7-dihydroxy-2-methylquinoline, m.p. 267—268°, unstable particularly in alkali [hydrochloride, +0.5H<sub>2</sub>O, m.p. 233° (decomp.); dibenzoate, m.p. 151—152°]. Boiling HI converts (II) into 6 : 7-dihydroxy-2-phenylquinoline, m.p. 275° (methiodide, m.p. 195°; dibenzoate, m.p. 177—178°), which with *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> (VI) at 210—220° gives 2'-phenylpyridino-6' : 5'-2 : 3-phenazine, m.p. 212—213°. *o*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH and quinoline at 250—260° give 2'-phenylpiperidino-6' : 5'-3 : 4-phenoxazine, m.p. 240—242°. S, Se, or SeO<sub>2</sub> gives indefinite products from (IV), but PhCHO and ZnCl<sub>2</sub> at 160° give the 4-CHPh derivative, m.p. 132°; the 4-phthalylidene derivative, m.p. 219°, is also detailed. Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, (IV), and K in Et<sub>2</sub>O-EtOH at 100° and then room temp. give Et 6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydroacridine-4-glyoxylate, m.p. 208—209°, converted by HI at 140° into 6 : 7-dihydroxy-1 : 2 : 3 : 4-tetrahydroacridine, m.p. 325° (dibenzoate, m.p. 170—171°), which with (VI) at 210° gives 5 : 6 : 7 : 8-tetrahydroquinolino-2 : 3-2' : 3'-phenazine, m.p. 350°. R. S. C.

**Conversion of  $\Delta^2$ -cyclohexenones and cyclohexanones into spirohydantoin.** H. R. Henze, R. C. Wilson, and R. W. Townley (*J. Amer. Chem. Soc.*, 1943, 65, 963—965).—The appropriate substituted cyclohexanones with KCN and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in aq. EtOH give 3 : 5-dimethyl-, m.p. 335—336°, 3-methyl-5-ethyl- (I), m.p. 282° (decomp.), 3-phenyl-5-methyl- (II), m.p. 223—224°, and 3-2'-furyl-5-methyl-, m.p. 223—224° (decomp.), -cyclohexane-1-spiro-4'-hydantoin.  $\Delta^2$ -cyclohexenones (A) also add HCN, thus yielding 3-cyano-3 : 5-dimethyl-, m.p. 196—197°, 3-methyl-5-ethyl-, m.p. 173—174°, 5-phenyl-3-methyl-, m.p. 221°, and 5-2'-furyl-3-methyl-, m.p. 210—211° (after resolidification, remelts at 215°), -cyclohexane-1-spiro-4'-hydantoin. Treating (A) with alkali sulphite and then with KCN etc. gives 3-sulpho-3 : 5-dimethyl- (K salt), 3-methyl-5-ethyl-, m.p. 175° (decomp.) (K salt), 5-phenyl-3-methyl-, m.p. 273—275° (decomp.), and 5-2'-furyl-3-methyl-cyclohexane-1-spiro-4'-hydantoin (K salt). Na-C<sub>5</sub>H<sub>11</sub>-OH reduces (I) to 3-methyl-5-ethyl-3-aminomethylcyclohexane-1-spiro-4'-hydantoin, m.p. 223°. Hydrogenating (PtO<sub>2</sub>) (A) [prep. from CH<sub>3</sub>Ac·CO<sub>2</sub>Et (2 mols.), RCHO (1 equiv.), and a little NH<sub>4</sub>Et<sub>2</sub>] in EtOH at 2 atm. gives 3 : 5-dimethyl-, b.p. 181—182°/750 mm. (semicarbazone, m.p. 220—200.5°), 3-methyl-5-ethyl-, b.p. 204—205°/747 mm. (semicarbazone, m.p. 189—190°), 3-phenyl-5-methyl-, b.p. 180—181°/26 mm. (semicarbazone, m.p. 111.5—112°), and 3-2'-furyl-5-methyl-cyclohexanone, b.p. 147—148°/22 mm. (semicarbazone, m.p. 172—173°). (I) is neither hypnotic nor anticonvulsant. (II) is mildly convulsant. SO<sub>3</sub>H or 2-furyl reduces the toxicity but does not enhance the activity. M.p. are corr. R. S. C.

**Vinylalkylmalonic esters and barbituric acids.** (Miss) D. Heyl and A. C. Cope (*J. Amer. Chem. Soc.*, 1943, 65, 669—673).—CH<sub>2</sub>Br·CHBr·OEt, CHBr<sup>a</sup>(CO<sub>2</sub>Et)<sub>2</sub> (I), and Na (or NaNH<sub>2</sub>) in Et<sub>2</sub>O-xylene at -10° give CH<sub>2</sub>Br·CH(OEt)·CBu<sup>a</sup>(CO<sub>2</sub>Et)<sub>2</sub>, which when distilled (after or without boiling with Zn in EtOH) yields EtBr and  $\alpha$ -carbethoxy- $\beta$ -ethoxy- $\alpha$ -n-butyl- $\gamma$ -butyrolactone (II) (56%), b.p. 129—130°/2 mm., and 27% of unchanged (I). CH<sub>2</sub>Et(CO<sub>2</sub>Et)<sub>2</sub> gives similarly  $\alpha$ -carbethoxy- $\beta$ -ethoxy- $\alpha$ -ethyl- $\gamma$ -butyrolactone (66%), b.p. 149.5°/8.5 mm. CH<sub>2</sub>Cl·CHCl·OEt, (I), and Na in Et<sub>2</sub>O at -10° and then 0° give Et<sub>2</sub>  $\beta$ -chloro- $\alpha$ -ethoxyethylmalonate (68%), b.p. 119°/2 mm., which is more stable but from which HCl could not be removed by Zn-EtOH. CMePr<sup>a</sup>·C(CN)<sub>2</sub> and H<sub>2</sub>-Pd-C in EtOH at 1—2 atm. give  $\alpha$ -methyl-n-butylmalononitrile [ $\alpha$ -cyano- $\beta$ -methyl-n-hexonitrile] (67%), b.p. 99—100°/8 mm., which could not be alkylated as it gives no Na derivative. CHMePr<sup>a</sup>·CH(CN)·CO<sub>2</sub>Et similarly resists alkylation. With CO(NH<sub>2</sub>)<sub>2</sub> and NaOEt in boiling EtOH, (II) gives 5- $\beta$ -hydroxy- (III) (60%), m.p. 127—127.5°, and thence (SOCl<sub>2</sub>-C<sub>5</sub>H<sub>5</sub>N-CCl<sub>4</sub>) 5- $\beta$ -chloro- (IV) (95%), m.p. 158.5—159°, and (SOBr<sub>2</sub>-C<sub>5</sub>H<sub>5</sub>N-C<sub>6</sub>H<sub>6</sub>) 5- $\beta$ -bromo- (V) (80%), m.p. 166—167°, - $\alpha$ -ethoxyethyl-5-n-butylbarbituric acid. Boiling 48% HBr converts (III), (IV), or (V) into 5-n-butylbarbituric acid, probably by way of the 5-epoxyethyl and 5-Ac derivatives. Dehalogenation of, e.g., 1-C<sub>10</sub>H<sub>7</sub>Br at 230° (69% yield of C<sub>10</sub>H<sub>8</sub>) by Zn is improved by operating in NH<sub>2</sub>Ac; this method is applied to  $\beta$ -bromovinylmalonic esters. Thus, CHBr·CH·CEt(CO<sub>2</sub>Et)<sub>2</sub> and Zn dust in NH<sub>2</sub>Ac at 180° give 71% of CH<sub>2</sub>·CH·CEt(CO<sub>2</sub>Et)<sub>2</sub>, b.p. 117.5—118°/22 mm., which with guanidine carbonate and NaOEt (excess avoided) in boiling EtOH and then boiling aq. HCl gives 29% of 5-ethyl-5-vinylbarbituric acid (VI), m.p. 172.5—173°. Adding, successively, iso-C<sub>5</sub>H<sub>11</sub>·CH(CO<sub>2</sub>Et)<sub>2</sub>, a little EtOH, and (CHBr)<sub>2</sub> to NaNH<sub>2</sub> (prepared *in situ*) in Et<sub>2</sub>O and then boiling gives Et<sub>2</sub> isoamyl- $\beta$ -bromovinylmalonate (38% + a residue), b.p. 158°/11 mm. [omission of the EtOH (? function) reduces the yield to 5%], which with Zn in boiling NH<sub>2</sub>Ac give Et<sub>2</sub> isoamylvinylmalonate (72%), b.p. 125—126°/10 mm., and thence, as above, 5-isoamyl-5-vinylbarbituric acid (VII) (32%), m.p. 129.5—130°. (CHBr)<sub>2</sub>, (I), and Na in Et<sub>2</sub>O

give similarly Et<sub>2</sub> n-butyl- $\beta$ -bromovinyl- (26%), b.p. 149°/10 mm., and -vinyl-malonate (70%), b.p. 116—117°/9 mm., and 5-n-butyl-5-vinylbarbituric acid (VIII) (40%), m.p. 84—85°. (CHBr)<sub>2</sub>, CH<sub>2</sub>·CH·CH<sub>2</sub>·CH(CO<sub>2</sub>Et)<sub>2</sub>, EtOH (a little), and NaNH<sub>2</sub> in Et<sub>2</sub>O give Et<sub>2</sub>  $\beta$ -bromovinylallylmalonate [Et  $\alpha$ -carbethoxy- $\alpha$ - $\beta$ -bromovinyl- $\Delta^2$ -n-pentenoate] (IX) (26%), b.p. 101°/2 mm., hydrogenated (Pd-C; EtOH) to CEtPr<sup>a</sup>(CO<sub>2</sub>Et)<sub>2</sub> (identified by hydrolysis and conversion into the barbituric acid) and converted by Zn dust in NH<sub>2</sub>Ac at 130—170° into Et<sub>2</sub> vinylallylmalonate (X) (39%), b.p. 112—113°/11 mm. Attempts to rearrange (IX) by heat result only in polymerisation. At 140° (X) is unchanged, at 200° it gives a mixture, but at 170° (8 hr.) gives ~30% of Et<sub>2</sub>  $\Delta^8$ -pentenylidenemalonate [Et<sub>2</sub>  $\alpha$ -carbethoxy- $\Delta^8$ -heptadienoate], b.p. 140—143°/6 mm., identified by hydrogenation (Pd-C-EtOH) to n-C<sub>5</sub>H<sub>11</sub>·CH(CO<sub>2</sub>Et)<sub>2</sub> (derived diamide, m.p. 198—199°). The structures of (VI)—(VIII) are confirmed by quant. hydrogenation to the known dialkylbarbituric acids. The vinyl-acids, (VI)—(VIII), are less effective and have poorer therapeutic ratios than have the isomeric ethylalkylidenebarbituric acids. (III), (IV), and (V) are non-toxic and non-hypnotic (orally) at 800 mg. per kg. to mice. R. S. C.

**Barbituric acids.**—See B., 1943, II, 246.

**Pyrazolones.**—See B., 1943, II, 176.

**Pyrazole compounds. III. Condensation of  $\alpha$ -carbethoxyacetothioacetanilide with hydrazines.** A. Weissberger and H. D. Porter (*J. Amer. Chem. Soc.*, 1943, 65, 732—734; cf. A., 1943, II, 207).—Boiling CHNaAc·CO<sub>2</sub>Et and PhNCS in MeOH, adding 85% N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O at 50°, and boiling again gives 3-anilino-5-pyrazolone, m.p. 268—270° (decomp.; rapid heating), also obtained by interaction in two steps [Worrall, A., 1918, i, 161; 1922, i, 874; m.p. 255—256° (decomp.); ? dimorphism]. Use of NHPh·NH<sub>2</sub> gives 5-anilo-3-hydroxy-1-phenylpyrazole (I) (30%), m.p. 168—169°, also obtained from 5-imino-3-hydroxy-1-phenylpyrazoline (II) in boiling NH<sub>2</sub>Ph. Use of NHMe·NH<sub>2</sub> gives 5-anilo-3-hydroxy-1-methylpyrazole (III) (2%), m.p. 208—209°, and 3-anilino-1-methyl-5-pyrazolone (IV) (11.5%), m.p. 220—222°. Oxidation in presence of *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub> gives a weak, dull bluish-magenta colour from (II), (I), or (III), but a brilliant magenta colour from 3-amino- (V) or 3-anilino-1-phenyl-5-pyrazolone (VI) or (IV). Similarly, (IV), (V), and (VI) give deep red azomethine dyes with *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub> in boiling EtOH, but (I), (II), and (III) are not affected. R. S. C.

**Pyrazoles.**—See B., 1943, II, 203.

**New synthesis of 3-carboline (norharman) and 5-carboline.** E. Späth and K. Eiter (*Ber.*, 1940, 73, [B], 719—723).—3-Bromopyridine, *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, and H<sub>2</sub>O + a little CuSO<sub>4</sub> at 155° for 9 hr. (sealed tube) give N-3-pyridyl-*o*-phenylenediamine, m.p. 125.5—126°, converted by aq. HCl-NaNO<sub>2</sub> into 1-3'-pyridylbenztriazole (I), m.p. 136.5—137°, which at ~350° for 8 hr. gives 3-carboline (II) (norharman), m.p. 198.5°. (I) and ZnCl<sub>2</sub> at 320° (15 min.) yield (II), 3-anilinopyridine, m.p. 142° (also obtained from 3-aminopyridine, PhI, and Cu-K<sub>2</sub>CO<sub>3</sub> in boiling *p*-toluidine at 200° for 15 hr.), and 5-carboline, m.p. 214—215° [also obtained from (I) at ~350° for 12 hr.] (for nomenclature, cf. Gulland *et al.*, A., 1930, 219).

A. T. P.

**Polynuclear condensed systems with heterocyclic rings. XII. 3-Phenyl-1 : 2-diaza-anthrone and other pyridazine derivatives.** W. Borsche and A. Klein (*Annalen*, 1941, 548, 74—81).—N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O and CH<sub>2</sub>Ph·CO·CH(CH<sub>2</sub>Bz)·CO<sub>2</sub>Et in EtOH at room temp. give the dihydrazone, m.p. 162—163°, or, after longer heating, Et 6-phenyl-3-benzyl-4 : 5-dihydropyridazine-4-carboxylate, m.p. 115°, oxidised by CrO<sub>3</sub> in warm AcOH to Et 6-phenyl-3-benzylpyridazine-4-carboxylate, m.p. 77—78°. The derived acid, m.p. 195—196° (decomp.), at 200—210° gives CO<sub>2</sub> and 3-phenyl-6-benzylpyridazine, m.p. 142°, and with SOCl<sub>2</sub> and then AlCl<sub>3</sub>-PhNO<sub>2</sub> at 50—60° gives 3-phenyl-1 : 2-diaza-9-anthrone, m.p. 236° (2 : 4-dinitrophenylhydrazone, m.p. 244°). CH<sub>2</sub>Bz·CHBz·CO<sub>2</sub>Et and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in EtOH at room temp. give Et 3 : 6-diphenyl-4 : 5-dihydropyridazine-4-carboxylate, m.p. 118°, and thence, as above, 3 : 6-diphenylpyridazine-4-carboxylic acid, m.p. 221° (Et ester, m.p. 100°), the chloride from which yields the anilide, m.p. 206°, but cannot be cyclised. CH<sub>2</sub>Ph·CHAc·CO<sub>2</sub>Et gives similarly Et 6-phenyl-3-methyl-4 : 5-dihydropyridazine-4-carboxylate, m.p. 98°, and 6-phenyl-3-methylpyridazine-4-carboxylic acid, m.p. 201° (decomp.), thermal decomp. of which gives 6-phenyl-3-methylpyridazine, m.p. 104—105°. With RCHO this gives 6-phenyl-3-styryl-, m.p. 184°, and -3-*p*-methoxystyryl-pyridazine, m.p. 200°. Et 2-carboxylamido-6-phenyl-3-methyl-2 : 5-dihydropyridazine-4-carboxylate (A., 1904, i, 778) with boiling KOH-MeOH-H<sub>2</sub>O gives the derived acid, m.p. 254° (decomp.), which at ~260° gives 6-phenyl-3-methyl-2 : 5-dihydropyridazine-2-carboxylamide, m.p. 147°; the CO·NH<sub>2</sub> resists hydrolysis. An isomeric substance, C<sub>12</sub>H<sub>13</sub>ON<sub>2</sub>, m.p. ~235° after decomp., is obtained (Spannagel, *Diss.*, 1903) from COMe·CH<sub>2</sub>Bz and NH<sub>2</sub>·CO·NH·NH<sub>2</sub>. R. S. C.

**Methylation of hydroxyl groups in triazines.** H. Sobotka and E. Bloch (*J. Mt. Sinai Hosp.*, 1942, 8, 1032—1033; cf. A., 1938, II, 70).—Attempts to methylate or acetylate the OH of 2-hydroxy-

4 : 6-diketo-2-alkyl- (or -phenyl)-1 : 3 : 5-trimethylhexahydrotriazine were unsuccessful. E. M. J.

**Insect dyes. VIII. Leucopterin.** C. Schöpf and R. Reichert [with K. Riefstahl] (*Annalen*, 1941, 458, 82—94).—The structure of leucopterin (I) as 2-imino-6 : 8 : 9-trihydroxypteridine is confirmed. This and similar CO compounds are named as (enolic) OH-derivatives of pteridine (II). Purification of (I) (Na salt) as *K* salt is described. Deiminoleucopterin (III) (prep. from 4 : 5-diamino-2 : 6-dihydroxypyrimidine sulphate,  $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , and cryst. NaOAc at 160° rising to 260°) with  $\text{PCl}_5$ — $\text{POCl}_3$  at 110° gives 2 : 6 : 8 : 9-tetrachloropteridine (IV), m.p. 161°, not reducible but converted by 25% NaOH at 140° into (III), by 0.75*N*-NaOH at 80° or *N*-LiOH at room temp. or 100° into 2 : 6-dichloro-8 : 9-dihydroxypteridine (V),  $+1.5\text{H}_2\text{O}$ , m.p. 260—270° (decomp.), and by dry  $\text{NH}_3$ — $\text{Et}_2\text{O}$  into trichloro-*x*-aminopteridine (33%), m.p. 197—201° (decomp.). Prep. of (V) from (III) by  $\text{PCl}_5$  under less careful conditions is thus due to lability of two Cl of the intermediate (IV). R. S. C.

**Preparation of flavins.** H. Lettré and M. E. Fernholz (*Ber.*, 1940, 73, [B], 436—441).— $\beta\text{-C}_{10}\text{H}_7\text{-NHPh}$  is coupled with diazotised  $\text{NH}_2\text{Ph}$ , and the azo-dye is reduced ( $\text{Na}_2\text{S}_2\text{O}_4$ ) to 1 : 2- $\text{NH}_2\text{-C}_{10}\text{H}_6\text{-NHPh}$ , m.p. 124—126°, which is condensed with alloxan and  $\text{H}_3\text{BO}_3$  in AcOH to 9-phenyl-5 : 6-benzoflavin, m.p. >365° (decomp.). Similar methods are used in the prep. of the following -5 : 6-benzoflavins : 9-phenyl-3-methyl-, m.p. >365°, incipient decomp. 335°; 9- $\beta$ -naphthyl-, m.p. ~357° after decomp.; 9-methyl-, m.p. >365°; 9-ethyl-, m.p. 326°; 9-*n*-propyl-, m.p. 319—320°; 9-*n*-butyl-, m.p. 297—298°; 9-isoamyl-, m.p. 273°; 9-*n*-hexyl-, m.p. 274—275°; 9-*n*-octyl-, m.p. 248—249°; 9-*n*-decyl-, m.p. 230°; 9-*n*-dodecyl-, m.p. 236°; 9-cetyl-, m.p. 221—222°; 3-methyl-9-cetyl-, m.p. 187—188°. All these compounds are sparingly sol. in  $\text{H}_2\text{O}$  but the simpler members are freely sol. in alkali. With increasing chain length they pass more and more completely into the  $\text{CHCl}_3$  layer when distributed between  $\text{CHCl}_3$  and aq. alkali. From this viewpoint their carcinogenic properties are investigated.  $\beta$ -Naphthyl-butyl-, m.p. 177—178°, and -cetyl-amine hydrobromide, m.p. 143—145°, 1-benzeneazo- $\beta$ -cetylnaphthylamine, m.p. 61°, and 1-amino-2-cetylaminonaphthalene hydrochloride, m.p. 144°, are incidentally described. H. W.

**Bile pigments. XXVII. Synthesis of 5 : 5'-diamino-4 : 4'-dimethyl-3 : 3'-diethylpyrromethene.** H. Fischer and H. Guggemos (*Z. physiol. Chem.*, 1939, 262, 37—46).—Et cryptopyrrolecarboxylate is converted by excess of Br in AcOH at 60—70° into Et, 4 : 4'-dimethyl-3 : 3'-diethylpyrromethene-5 : 5'-dicarboxylate, m.p. 132—134°. 4 : 4'-Dimethyl-3 : 3'-diethylpyrromethane-5 : 5'-dicarboxylhydrazide, m.p. 238°, best obtained from Et, 4 : 4'-dimethyl-3 : 3'-diethylpyrromethane-5 : 5'-dicarboxylate and boiling  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , is converted by  $\text{NaNO}_2$  in AcOH at 0° into the diazide (I), m.p. 127° (decomp.), transformed by  $\text{NH}_2\text{Ph}$  at 140° into the 5 : 5'-di(phenylcarbamide), m.p. 235°, and by Zn dust at AcOH into the 5 : 5'-dicarboxylamide, m.p. 300°. (I) is transformed by Br in  $\text{Et}_2\text{O}$  into 4 : 4'-dimethyl-3 : 3'-diethylpyrromethene-5 : 5'-dicarboxazide (II), m.p. 130° (decomp.) [hydrobromide, m.p. 133° (decomp.)], which with boiling EtOH yields the -5 : 5'-diethylurethane, m.p. 147° (4 : 4'-dimethyl-3 : 3'-diethylpyrromethane-5 : 5'-diethylurethane has m.p. 124—125°). (II) is converted by boiling 50% AcOH into a non-cryst. material whereas (I) affords the -5 : 5'-diamine diacetate (III), m.p. (indef.) 185°, decomp. >135°. Hot 4% NaOH converts (III) into 5 : 5'-diamino-4 : 4'-dimethyl-3 : 3'-diethylpyrromethene, decomp. 157°, which very readily passes in air into  $\beta\delta$ -di-imino $\alpha$ tioporphyrin and is therefore analysed as the very stable complex,  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{Cu}$ , m.p. >350°. H. W.

**Chlorophylls. XCIV. Protochlorophyll and vinylporphyrins.** The oxo-reaction. H. Fischer and A. Oestreicher (*Z. physiol. Chem.*, 1939—40, 262, 243—269).—Adding  $\text{COCl}_2$  to vinylphæoporphyrin-*a*, Me H ester and phytol in  $\text{C}_5\text{H}_5\text{N}$  at 0° and then room temp. gives the Me phytol ester (protochlorophyllin) (I), m.p. ~144—146°. This is obtained in poor yield (owing to hydrolysis) by addition of Fe powder to vinylphæophytin in  $\text{COMe}_2$ —80%  $\text{HCO}_2\text{H}$  at 100°, reoxidation in air, and purification by adsorption. The colour and spectrum of (I) are the same as those of vinylphæoporphyrin-*a*, (II). Mg is introduced into (I) by  $\text{MgEtBr}$  decomposed by  $\text{PrOH}$  or  $\text{PrOH}$  (not MeOH or EtOH), yielding an amorphous protochlorophyll; this differs in absorption spectrum (max. at 599.5 and 548.8  $\text{m}\mu$ ) from the natural product, probably because the latter contains a definite amount of (I) (this is probably present as such in nature and not an artefact). When methylphæophorbide-*b*, oxime is treated with Fe powder in boiling 80%  $\text{HCO}_2\text{H}$ , reoxidised in air, and esterified by  $\text{CH}_3\text{N}_2$ — $\text{Et}_2\text{O}$ , the isocyclic ring is closed and the  $\text{C:N-OH}$  hydrolysed and reduced to  $\text{CH}_2\text{OH}$ , yielding vinylphæoporphyrin-*b*, 3-methanol Me<sub>2</sub> ester, m.p. 269°, the structure of which is proved by its absorption spectrum (max. at 563.7, 590.1, 523.7, and ~650  $\text{m}\mu$ ) resembling that of (II), by failure to give an oxime in cold  $\text{C}_5\text{H}_5\text{N}$ , addition of  $\text{CHN}_2$ — $\text{CO}_2\text{Et}$ , and opening of the isocyclic ring by  $\text{KOH}$ — $\text{EtOH}$  (spectroscopic proof). Simi-

larly, the oxime of rhodin-*g*, Me<sub>2</sub> ester gives vinylrhodinporphyrin-*g*, 3-methanol Me<sub>2</sub> ester (poor yield), which is also obtained in poor yield from vinylphæoporphyrin-*b*, 3-methanol Me<sub>2</sub> ester by  $\text{KOH}$ — $\text{MeOH}$ — $\text{C}_5\text{H}_5\text{N}$  at room temp. and has the same absorption spectrum as has vinylchloroporphyrin-*e*, (III). Hydrolysis of phæophytin-*a* + *b* by boiling  $\text{KOH}$ — $\text{MeOH}$ — $\text{COMe}_2$  (4 min.) gives oily *K* and thence solid Ba salts; phytol adsorbed thereon is extracted by  $\text{Et}_2\text{O}$  and readily purified; dissolving the residual salts in acid and extracting fractionally with  $\text{Et}_2\text{O}$  then yields pure chlorin-*e*, and impure rhodin-*g*. Two methods for prep. of (II) give only poor yields. 2-*a*-Hydroxychloroporphyrin-*e*, Me<sub>2</sub> ester, m.p. 247° (absorption max. at 445, 581.7, 544.8, and 633  $\text{m}\mu$ ), similar to those of chloroporphyrin-*e*, Me<sub>2</sub> ester, is obtained by treating the Me<sub>2</sub> ester of (III) with  $\text{HI}$ — $\text{AcOH}$  at room temp. and then reoxidising; at the m.p./high vac. it suffers ring-closure of the isocyclic ring with loss of MeOH, but with  $\text{P}_2\text{O}_5$  and sand at room temp. it gives (III); its prep. involves addition of  $\text{HI}$ , followed by hydrolysis; thus, it is also formed (m.p. 246°) when  $\text{HBr}$  is added to (III) in  $\text{AcOH}$  and the product is hydrolysed by 20%  $\text{HCl}$  at room temp. and finally esterified. Similarly, with, successively,  $\text{HBr}$ — $\text{AcOH}$  at 45°, 20%  $\text{HCl}$ , and  $\text{CH}_3\text{N}_2$ , vinylphylloerythrin Me<sub>2</sub> ester (IV) gives 2-*a*-hydroxyphylloerythrin Me<sub>2</sub> ester, m.p. ~284—286° (absorption max. at 562.5, 591.8, 522.3, and 641.2  $\text{m}\mu$ ), which with  $\text{P}_2\text{O}_5$  + sand regenerates (IV); it is also obtained from oxophylloerythrin by hydrogenating ( $\text{PtO}_2$ ;  $\text{HCO}_2\text{H}$ ) and then reoxidising and esterifying and is reconverted thereto by  $\text{I}$ — $\text{AcOH}$ . Further, treating vinylphæoporphyrin-*a*, Me<sub>2</sub> ester with  $\text{HI}$  in  $\text{AcOH}$  + a little  $\text{CHCl}_3$  at 12° for 2 days and esterifying the 2- $\text{CHMe-OH}$  fraction gives 2-*a*-hydroxyphæoporphyrin-*a*, Me<sub>2</sub> ester, m.p. 285° (absorption max. at 561.2, 588.9, 521.7, and 638.1  $\text{m}\mu$ ). Vinylchloroporphyrin-*e*, Me<sub>2</sub> ester (V), m.p. 254° [absorption max. at 510.7, 548.1, 586.2, and ~660  $\text{m}\mu$ ; Cu salt, m.p. 200° (absorption max. at 546.4 and 589.5  $\text{m}\mu$ ), reduced by  $\text{H}_2$ — $\text{Pd}$  in  $\text{COMe}_2$  to the leuco-compound of the Et compound and converted by  $\text{HI}$ — $\text{AcOH}$  into the Cu-free ester], is obtained from the -*e*, Me<sub>2</sub> ester by boiling  $\text{HCO}_2\text{H}$  and then  $\text{CH}_3\text{N}_2$ ; some (II) is also formed. (V) is also obtained by treating the chlorin-*e*, Me<sub>2</sub> ester with Fe powder in 80%  $\text{AcOH}$  at 100°, reoxidising the product with  $\text{FeCl}_3$ , and esterifying, but the yield is poor owing to decomp. of the leuco-compound.  $\text{I-KOAc}$  oxidises (V) to vinylchloroporphyrin-*e*, m.p. >320° (absorption max. at 558, 587.7, 516.2, and 635.2  $\text{m}\mu$ ). Phæophorbide-*a* is slowly converted into (II) by boiling with Fe dust and  $\text{H}_2\text{C}_2\text{O}_4$  in  $\text{COMe}_2$  and then reoxidising. The mechanism by which, in the changes described above, reduction and oxidation occur simultaneously at different parts of the mol. is inconclusively discussed. 2-*a*-Hydroxymeso-chlorin-*e*, Me<sub>2</sub> ester with  $\text{KMnO}_4$  in  $\text{C}_5\text{H}_5\text{N}$  at room temp. and then  $\text{CH}_3\text{N}_2$  gives 48% of acetylchlorin-*e*, Me<sub>2</sub> ester, which yields a Cu, m.p. 198°, [ $\alpha_{\text{white}}^{20}$  —1260° in  $\text{COMe}_2$  (absorption max. at 652.6, 507, 599.5, and 549  $\text{m}\mu$ ), Fe, m.p. 176—178°, [ $\alpha_{\text{white}}^{20}$  +2870° and [ $\alpha_{\text{red}}^{20}$  —1080° in  $\text{COMe}_2$  (absorption max. 625 and 488.1  $\text{m}\mu$ ), and Mn derivative, m.p. 170—173°, decomp. 185—190°, [ $\alpha_{\text{white}}^{20}$  +4300°, [ $\alpha_{\text{red}}^{20}$  —540° in  $\text{COMe}_2$  (absorption max. at 480.2, 682.8, and 437.2  $\text{m}\mu$ )]. R. S. C.

**Photo-oxidation of chlorophyll.**—See A., 1943, I, 206.

**Synthesis of isoquinoline derivatives. IV. Synthesis of oxazolines and isoquinolines from *N*-acylaminocarbinols.** W. Krabbe, W. Eisenlohr, and H. G. Schöne (*Ber.*, 1940, 73, [B], 656—660; cf. A., 1943, II, 263).— $\text{NHBz-CH}_2\text{-CPhMe-OH}$  and  $\text{H}_2\text{SO}_4$  at room temp. give 2 : 5-diphenyl-5-methyl- $\Delta^2$ -oxazoline (picrate, m.p. 145°), converted by boiling aq.  $\text{HCl}$  into  $\text{NHBz-CH-CHPhMe}$  and  $\text{BzOH}$ .  $\text{NHAc-CHPh-CPh}_2\text{-OH}$  and  $\text{P}_2\text{O}_5$  or  $\text{H}_2\text{SO}_4$  give 4 : 5 : 5-triphenyl-2-methyl- $\Delta^2$ -oxazoline (cf. acet- $\beta\beta$ -diphenylvinylamide, m.p. 166°; A., 1938, II, 111), rehydrolysed by acid or alkali. A. T. P.

**Sulphanilamide compounds. VIII. Homologues of 2-sulphanilamidothiazoline.** A. H. Nathan, J. H. Hunter, and H. G. Kolloff (*J. Amer. Chem. Soc.*, 1943, 65, 949—950; cf. A., 1941, II, 147).—2-Amino-4- and -5-methylthiazoline with *p*- $\text{NHAc-C}_6\text{H}_4\text{-SO}_2\text{Cl}$  in  $\text{C}_5\text{H}_5\text{N}$ — $\text{COMe}_2$  at <45° give 2-acetylsulphanilimido-3-acetylsulphanilyl-4-, + $\text{H}_2\text{O}$ , m.p. 150—153° (decomp.), and -5-, m.p. 185.5—186.5°, hydrolysed by boiling 10%  $\text{HCl}$  to 2-sulphanilimido-3-sulphanilyl-4-, m.p. 225—226°, and -5-, m.p. 176.5—177°, and then to 2-sulphanilamido-4-, m.p. 176°, and -5-, m.p. 177.5—178.5°, -methylthiazoline. R. S. C.

**Thiazoles.**—See B., 1943, II, 174.

**Benzthiazolium compounds.**—See B., 1943, II, 175, 246.

**Cyanine dyes.**—See B., 1943, II, 175, 178, 246, 247, 268.

## VII.—ALKALOIDS.

**Ergot alkaloids. IV. Optically active hydrazides of lysergic and isolysergic acid.** A. Stoll and A. Hofmann (*Helv. Chim. Acta*, 1943, 26, 922—928; cf. A., 1938, II, 35, 164).—*r*-isoLyserghydrazide (I), m.p. (indef.) 240° (decomp.), is obtained by the action of  $\text{N}_2\text{H}_4$

at 130—140° on any of the natural ergot alkaloids or mixtures thereof which does not belong to the ergobasine type. Finely-divided *d*-tartaric acid and *p*-C<sub>6</sub>H<sub>4</sub>Me·COCl at 120° afford *d*-*di*-*p*-toluoyl-tartaric anhydride, m.p. 197—198° (decomp.),  $[\alpha]_D^{20} + 195^\circ$  in COMe<sub>2</sub>, hydrolysed by boiling aq. COMe<sub>2</sub> to *d*-*di*-*p*-toluoyltartaric acid (II), m.p. 172° (decomp.),  $[\alpha]_D^{20} - 140^\circ$  in EtOH. 1-*Di*-*p*-toluoyltartaric anhydride,  $[\alpha]_D^{20} - 195^\circ$  in COMe<sub>2</sub>, and acid (III),  $[\alpha]_D^{20} + 140^\circ$  in EtOH, are obtained similarly. (I) and (III) in boiling MeOH give *d*-isolyserghydrazide *H* 1-*di*-*p*-toluoyltartrate (IV),  $[\alpha]_D^{20} + 328^\circ$  in MeOH, converted by NaHCO<sub>3</sub> into *d*-isolyserghydrazide (V), m.p. (indef.) 204° (decomp.),  $[\alpha]_D^{20} + 452^\circ$  in C<sub>5</sub>H<sub>5</sub>N. The base derived from the mother-liquors from (IV) is largely freed from (I) by treatment with EtOAc or preferably is treated with (II), thereby giving *l*-isolyserghydrazide, m.p. 204° (decomp.),  $[\alpha]_D^{20} - 454^\circ$  in C<sub>5</sub>H<sub>5</sub>N. (V) is isomerised by boiling H<sub>3</sub>PO<sub>4</sub>-EtOH or, preferably, by mild treatment with KOH-EtOH to *d*-lyserghydrazide, m.p. (indef.) 218° (decomp.),  $[\alpha]_D^{20} + 11^\circ$  in C<sub>5</sub>H<sub>5</sub>N. 1-Lyserghydrazide has m.p. 218° (decomp.),  $[\alpha]_D^{20} - 11^\circ$  in C<sub>5</sub>H<sub>5</sub>N. H. W.

**Ergot alkaloids. VI. Partial synthesis of alkaloids of the type of ergobasine.** A. Stoll and A. Hofmann (*Helv. Chim. Acta*, 1943, 26, 944—965).—The alkaloids are obtained by interaction of optically active lyserg- and isolyserg-azides with optically active NH<sub>2</sub>-alcohols. *d*-isoLyserghydrazide (I) in 0·1N-HCl at 0° is treated with NaNO<sub>2</sub> followed by NaHCO<sub>3</sub> and the liberated azide is extracted with Et<sub>2</sub>O. The dried ethereal solution is kept at room temp. for a day in the dark with *l*(+)-NH<sub>2</sub>·CHMe·CH<sub>2</sub>·OH (2 mols.), thus giving *d*-isolyserg- $\alpha$ -hydroxyisopropylamide (ergobasine) (II); the mother-liquors from (II) afford *d*-lyserg- $\alpha$ -hydroxyisopropylamide (III) when treated with CHCl<sub>3</sub>. (II) is isomerised to (III) by KOH-aq. EtOH at room temp. The pre-isomerisation of (I) to *d*-lyserghydrazide and thus the direct production of (III) is not advisable since some back-isomerisation always occurs. Similarly obtained are *d*-isolyserg- $\alpha$ -hydroxyisopropylamide, m.p. 195° (decomp.),  $[\alpha]_D^{20} + 353^\circ$  in CHCl<sub>3</sub> (perchlorate), and *d*-lyserg- $\alpha$ -hydroxyisopropylamide, m.p. 220° (decomp.),  $[\alpha]_D^{20} - 11^\circ$  in C<sub>5</sub>H<sub>5</sub>N [*H* oxalate, m.p. 190—195° (decomp.),  $[\alpha]_D^{20} + 58^\circ$  in H<sub>2</sub>O]; *l*-isolyserg- $\alpha$ -hydroxyisopropylamide, m.p. 192—195° (decomp.),  $[\alpha]_D^{20} - 351^\circ$  in CHCl<sub>3</sub> (perchlorate), and *l*-lyserg- $\alpha$ -hydroxyisopropylamide, m.p. 220° (decomp.),  $[\alpha]_D^{20} + 10^\circ$  in C<sub>5</sub>H<sub>5</sub>N [*H* oxalate, m.p. 192° (decomp.),  $[\alpha]_D^{20} - 59^\circ$  in H<sub>2</sub>O] (photomicrographs of the derivatives of NH<sub>2</sub>·CHMe·CH<sub>2</sub>·OH are given). *d*-isoLyserg-, m.p. 204—206° (decomp.),  $[\alpha]_D^{20} + 448^\circ$  in C<sub>5</sub>H<sub>5</sub>N, and *d*-lyserg- (+)CHCl<sub>3</sub>, m.p. 95° (decomp.), (solvent free)  $[\alpha]_D^{20} - 10^\circ$  in C<sub>5</sub>H<sub>5</sub>N,  $\beta$ -hydroxyethylamide; *d*-isolyserg-, m.p. 192—194° (decomp.),  $[\alpha]_D^{20} + 386^\circ$  in CHCl<sub>3</sub>, and *d*-lyserg- $\alpha$ -hydroxy- $\beta$ -n-butylamide, m.p. 172° (decomp.),  $[\alpha]_D^{20} - 45^\circ$  in C<sub>5</sub>H<sub>5</sub>N (tartrate) [methylelbergobasine and methylelbergobasine]; *d*-isolyserg-, m.p. 160° (decomp.),  $[\alpha]_D^{20} + 330^\circ$  in CHCl<sub>3</sub>, and *d*-lyserg-*l*(+)- $\alpha$ -hydroxy- $\delta$ -methyl- $\beta$ -n-amylamide (+C<sub>6</sub>H<sub>5</sub>), m.p. indef. 130°, or + COMe<sub>2</sub>, m.p. 120—130°,  $[\alpha]_D^{20} - 38^\circ$  in C<sub>5</sub>H<sub>5</sub>N [isopropyl-ergobasine and -ergobasine]; *d*-isolyserg- (+)Et<sub>2</sub>O, m.p. 125—130° (decomp.),  $[\alpha]_D^{20} + 267^\circ$  in COMe<sub>2</sub>, and *d*-lyserg-*d*-norephedrine,  $[\alpha]_D^{20} + 14^\circ$  in COMe<sub>2</sub> (hydrochloride, decomp. 230°, darkens at 200°); *l*-isolyserg- and *l*-lyserg-*l*-norephedrine, non-cryst.,  $[\alpha]_D^{20} - 16^\circ$  in COMe<sub>2</sub> (hydrochloride, decomp. 230°, darkens above 200°); *d*-isolyserg- and *d*-lyserg-*l*-norephedrine (+)C<sub>6</sub>H<sub>5</sub>, m.p. 130° (decomp.),  $[\alpha]_D^{20} - 17^\circ$  in COMe<sub>2</sub> [*d*-tartrate (+)MeOH], m.p. 185—200° (decomp.),  $[\alpha]_D^{20} + 39^\circ$  in 50% EtOH; non-cryst. *d*-isolyserg-,  $[\alpha]_D^{20} + 370^\circ$  in COMe<sub>2</sub>, and *d*-lyserg-*d*-nor- $\psi$ -ephedrine (+)C<sub>6</sub>H<sub>5</sub>, m.p. 131°,  $[\alpha]_D^{20} + 27^\circ$  in COMe<sub>2</sub>; *d*-isolyserg-, m.p. 231° (decomp.),  $[\alpha]_D^{20} + 445^\circ$  in C<sub>5</sub>H<sub>5</sub>N, and *d*-lyserg- $\alpha$ -*di*hydroxy- $\beta$ -propylamide (+)CHCl<sub>3</sub>, m.p. (indef.) 125° [*H* oxalate,  $[\alpha]_D^{20} + 55^\circ$  in H<sub>2</sub>O] [hydroxy-ergobasine and -ergobasine]; *d*-isolyserg-, m.p. 163°,  $[\alpha]_D^{20} + 396^\circ$  in C<sub>5</sub>H<sub>5</sub>N, and *d*-lyserg- $\beta$ -diethylaminoethylamide, non-cryst.,  $[\alpha]_D^{20} - 16^\circ$  in C<sub>5</sub>H<sub>5</sub>N [*H* oxalate, decomp. 200°,  $[\alpha]_D^{20} + 79^\circ$  in 50% EtOH]; *d*-lyserg-, m.p. 80—85°,  $[\alpha]_D^{20} + 30^\circ$  in C<sub>5</sub>H<sub>5</sub>N, and *d*-isolyserg-diethylamide, m.p. 182° (decomp.),  $[\alpha]_D^{20} + 217^\circ$  in C<sub>5</sub>H<sub>5</sub>N; *d*-lysergbenzyl- $\alpha$ -hydroxyisopropylamide [*N*-benzylelbergobasine], m.p. 230° (decomp.),  $[\alpha]_D^{20} - 17^\circ \pm 5^\circ$  in C<sub>5</sub>H<sub>5</sub>N; *d*-lyserg-*l*-ephedrine, m.p. 258° (decomp.),  $[\alpha]_D^{20} - 21^\circ$  in C<sub>5</sub>H<sub>5</sub>N. A brief survey of the physiological activity of the compounds shows that configurative differences may have a much more pronounced influence than marked differences in constitution. H. W.

## VIII.—ORGANO-METALLIC COMPOUNDS.

**Arsenicals derived from acetophenone.** R. L. Clark and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1943, 65, 635—637).—Adding Cl<sub>2</sub> (0·172 mol.) at ~40° to *p*-COMe·C<sub>6</sub>H<sub>4</sub>·AsCl<sub>2</sub> in EtOH and treating the product with H<sub>2</sub>O<sub>2</sub> gives  $\omega$ -chloro-*p*-arsonoacetophenone (I) (76%), m.p. 204—205° (208—209°) (A., 1938, II, 36, m.p. 189°) (semicarbazone, darkens 215°; oxime, m.p. 173—173·5°), converted by NHPH·NH<sub>2</sub>·HCl-NaHCO<sub>3</sub>-H<sub>2</sub>O at 100° into 1-phenyl-3-*p*-arsonophenyl-1:2-diaza- $\Delta^2$ -cyclobutene (35%), darkens 210—215°. With boiling HCO<sub>2</sub>K-MeOH-H<sub>2</sub>O, (I) gives  $\omega$ -hydroxy-*p*-arsonoacetophenone (16%), cryst. (cryst. semicarbazone and phenylhydrazine), reduced by KI-SO<sub>2</sub>-N-HCl to  $\omega$ -hydroxy-*p*-arsonoacetophenone (65%), cryst. The appropriate *sec.* amine and (I) in boiling MeOH give  $\omega$ -diethyl-

amino- (33%), m.p. 186—187°,  $\omega$ -morpholino- (63%), m.p. 172—173°, and  $\omega$ -piperidino-*p*-arsonoacetophenone hydrochloride (61%), m.p. 186—187°. R. S. C.

**Amidino-arsenicals. I. *p*-Amidinophenylarsonic acid and *pp'*-diamidinoarsenobenzene.** F. Linsker and M. T. Bogert (*J. Amer. Chem. Soc.*, 1943, 65, 932—934).—*p*-CN·C<sub>6</sub>H<sub>4</sub>·AsO<sub>3</sub>H<sub>2</sub> (I) [prep. from the NH<sub>2</sub>-acid (II) by a diazo-reaction in 82% yield] with HCl-EtOH-Et<sub>2</sub>O at 0° gives the imino-ether hydrochloride (74%), converted by 10% NH<sub>3</sub>-EtOH at 60° into *p*-amidinophenylarsonic acid [by way of its hydrochloride (84%), m.p. 280° (decomp.)], which, with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>-NaOH-MgCl<sub>2</sub>-H<sub>2</sub>O at room temp. and later 55—60° gives *pp'*-diamidinooarsenobenzene dihydrochloride, +4H<sub>2</sub>O, m.p. 240° (decomp.). Similar reduction of (I) or (II) gives impure *pp'*-dicyanoarsenobenzene, decomp. >260°, which with HCl-Et<sub>2</sub>O-NH<sub>3</sub> and then NH<sub>3</sub>-EtOH at 40° gives *p*-amidino-*p'*-cyanoarsenobenzene hydrochloride, +EtOH, darkens ~225°, m.p. ~234° (decomp. from 229°). R. S. C.

**Metallation of sulphur-containing organic compounds.** F. J. Webb (*Iowa State Coll. J. Sci.*, 1942, 17, 152—154).—The reactions of sulphides, disulphides, sulphoxides, and sulphones with Na, NaNH<sub>2</sub>, Hg<sup>II</sup> salts, and organometallic compounds are reviewed. Metallation of the sulphides RMeS (where R is *p*-C<sub>6</sub>H<sub>4</sub>Me, *p*-C<sub>6</sub>H<sub>4</sub>Cl, *p*-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>, and  $\alpha$ - and  $\beta$ -C<sub>10</sub>H<sub>7</sub>) by LiBu<sup>a</sup> in Et<sub>2</sub>O, followed by treatment with CO<sub>2</sub>, gives 38·2, 5·75, 22·4, 35·4, and 11·7% respectively of the corresponding arylthiolacetic acids. *p*-Dimethylaminophenylthiolacetic acid has m.p. 85—86°. PhEtS with LiBu<sup>a</sup> in Et<sub>2</sub>O, followed by CO<sub>2</sub>, gives ~8% of *o*-SEt·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H. Similarly PhPr<sup>a</sup>S, PhBu<sup>a</sup>S, and PhPr<sup>b</sup>S yield 6·9% of *o*-*n*-propyl-, 6—10% of *o*-*n*-butyl-, (I), and 11% of *o*-iso-propyl-thiolbenzoic acid, m.p. 116—117°. A similar reaction with Ph cyclohexyl sulphide yields an acid, m.p. 80—81°, probably *o*-cyclohexylthiolbenzoic acid. Each of the above reactions, except that with PhPr<sup>a</sup>S, yields a small amount of BzOH owing to cleavage of the Ph-S linking. Usually lateral exceeds nuclear metallation, and formation of BzOH does not occur. PhMeS and PhEtS are not metallated by CaPhI in Et<sub>2</sub>O. Hg(OAc)<sub>2</sub> with excess of PhMeS at 100° gives 36·6% of *p*-acetoxymercuriphenyl Me sulphide, m.p. 184°. LiMe and LiPh in Et<sub>2</sub>O, and LiBu<sup>a</sup> in light petroleum (b.p. 28—38°), and NaPh in C<sub>6</sub>H<sub>6</sub> react with PhMeS giving SPh·CH<sub>2</sub>·CO<sub>2</sub>H (II) after CO<sub>2</sub>-action, but MgBu<sup>a</sup>Br and PhMeS at 150—155° for 5 hr. yield, after CO<sub>2</sub>-action, 0·2% of *o*-SMe·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H. A similar high-temp. reaction between LiBu<sup>a</sup> and PhMeS gives 21·2% of SPh·CH<sub>2</sub>·CO<sub>2</sub>H, which indicates that it is the metallating agent and not temp. or solvent which governs the position of substitution in PhMeS. PhMeS with Na in Et<sub>2</sub>O gives 20·9% of PhSH and 3·45% of (I) subsequent to CO<sub>2</sub>-treatment and hydrolysis, whilst scarcely any cleavage occurs in C<sub>6</sub>H<sub>6</sub>. PhBu<sup>a</sup>S in Et<sub>2</sub>O and Li yield 11·9% of BzOH, 20·5% of PhSH, and 0·24% of (II). PhSH and (PhS)<sub>2</sub> are metallated by LiBu<sup>a</sup> to give, after CO<sub>2</sub>-action, (*o*-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·S)<sub>2</sub>. PhMeS is metallated slightly more readily than PhOMe by LiBu<sup>a</sup> in Et<sub>2</sub>O. *p*-C<sub>6</sub>H<sub>4</sub>Br·SMe does not form an org. Li compound under the usual conditions, and the main result of reaction with LiBu<sup>a</sup> is halogen-metal interconversion. With LiMe, mainly coupling occurs, with slight interconversion. PhSO<sub>2</sub>Me is metallated by LiBu<sup>a</sup>, yielding 47% of PhSO<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>H after CO<sub>2</sub>-action. PhSO<sub>2</sub>Et reacts vigorously with MgEtBr and with LiBu<sup>a</sup>, and Ph<sub>2</sub>SO<sub>2</sub> and dibenzthiophen 5-dioxide with LiBu<sup>a</sup> to yield unidentified acids. PhMeSe in Et<sub>2</sub>O with LiBu<sup>a</sup>, followed by CO<sub>2</sub>, give 28·4% of BzOH and MeBu<sup>a</sup>Se. NaC<sub>5</sub>H<sub>11</sub>-*n* in light petroleum (b.p. 28—38°) causes 25% cleavage of PhMeSe in 4 hr. at room temp. J. N. A.

**Reactions of organometallic compounds with alkyl halides. I. Action of sodium ethyl on (—)- $\beta$ -bromo-octane.** N. G. Brink, J. F. Lane, and E. S. Wallis (*J. Amer. Chem. Soc.*, 1943, 65, 943—949).—(—)- $\beta$ -Bromo-*n*-octane,  $[\alpha]_D^{20} - 30·7^\circ$ , and NaEt in C<sub>6</sub>H<sub>12</sub> at ~-10° (later 0°) give a 9:12:16:1 (mol.) mixture of C<sub>8</sub>H<sub>18</sub>, C<sub>8</sub>H<sub>16</sub>,  $\gamma$ -methyl-*n*-nonane, b.p. 166·8—167·1°/769 mm.,  $[\alpha]_D^{25} - 0·23^\circ$  (97% racemised), and  $\eta$ -*dimethyl-n*-tetradecane, b.p. 275°,  $\alpha$  0. The reaction mechanism is discussed. R. S. C.

**Factors determining the course and mechanism of Grignard reagents. VII. Analysis of gases formed during the reaction of magnesium phenyl bromide with organic halides in presence of cobaltous halides.** M. S. Kharasch, D. W. Lewis, and W. B. Reynolds. **VIII. Effect of metallic halides on the reaction of Grignard reagents with aromatic acyl halides.** M. S. Kharasch, W. Nudenberg, and S. Archer. **IX. Effect of metallic halides on the reaction of organolithium compounds with organic halides.** M. S. Kharasch, D. W. Lewis, and W. B. Reynolds. **X. Oxidation of Grignard reagents: effect of metallic catalysts.** M. S. Kharasch and W. B. Reynolds. **XI. Effect of metallic halides on the reaction of Grignard reagents with vinyl halides and substituted vinyl halides.** M. S. Kharasch and C. F. Fuchs (*J. Amer. Chem. Soc.*, 1943, 65, 493—495, 495—498, 498—500, 501—504, 504—507; cf. A., 1943, II, 227).—VII. Only 5—10% interaction occurs between MgPhBr and RBr (R = Me, Et, Pr<sup>a</sup>, or Bu<sup>a</sup>) or Bu<sup>a</sup>Cl in 20 hr. in Et<sub>2</sub>O-N<sub>2</sub>, PhR but no Ph<sub>2</sub> being formed. In presence of 3—5 mol.-% of CoCl<sub>2</sub> interaction is rapid, necessitating adding the RBr gradually;

the extent of reaction is  $R = \text{Me } 90, \text{Et } 45, \text{Pr}^a 62, \text{Bu}^a 83\%$ , and  $\text{Bu}^v$ ? Of the  $\text{RBr}$  which reacts, the following amounts yield gas:  $R = \text{Me } 67, \text{Et } 80, \text{Pr}^a 66, \text{Bu}^a 73$ , and  $\text{Bu}^v 75\%$ , and approx. equiv. amounts of  $\text{Ph}_2$  (and some polyphenyls) are formed. The gases formed are: from  $\text{MeBr}$ ,  $\text{CH}_4$  62,  $\text{C}_2\text{H}_6$  18, and  $\text{C}_2\text{H}_4$  20%; from  $\text{EtBr}$ ,  $\text{C}_2\text{H}_6$  40 and  $\text{C}_2\text{H}_4$  60%; from  $\text{Pr}^a\text{Br}$ ,  $\text{C}_2\text{H}_6$  54 and  $\text{C}_2\text{H}_4$  46%; from  $\text{Bu}^a\text{Br}$ ,  $\text{C}_4\text{H}_{10}$  54 and  $\text{C}_4\text{H}_8$  46%; from  $\text{Bu}^v\text{Cl}$ , *iso*- $\text{C}_5\text{H}_{12}$  80 and  $-\text{C}_5\text{H}_{10}$  20%. The reaction mechanism is:  $\cdot\text{CoCl} + \text{RBr} \rightarrow \text{CoClBr} + \text{R}\cdot$ . Disproportionation, and not dimerisation, of  $\text{R}\cdot$  then occurs, since the saturated and unsaturated gases are in approx. equiv. amounts. With  $\text{Me}\cdot$ , capture of a  $\text{H}$  from the solvent is a fast reaction (giving  $\text{CH}_4$ ) and interaction with  $\text{Et}_2\text{O}$  a slow one [giving  $\text{MeOEt}$  and  $\text{Et}\cdot \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$ ]. The deficiency of *iso*- $\text{C}_5\text{H}_{10}$  is due to its rapid polymerisation.

VIII. Adding  $\text{MgPhBr-Et}_2\text{O}$  to  $\text{BzCl} + \text{CoCl}_2$  (2 mol.-%) in  $\text{Et}_2\text{O}$  at the b.p. gives  $\text{Ph}_2$  (56%),  $\text{COPh}_2$  (much),  $\text{EtOBz}$  (3%),  $\text{BzOH}$  (10%),  $\text{COPh}\cdot\text{CPh}_2\cdot\text{OH}$  (I) (11%),  $(\text{CPh}_2)_2\text{O}$  (II) (1%), and  $(\text{CPh}\cdot\text{OBz})_2$  (III) (3%). Use of 5 mol.-% of  $\text{CoCl}_2$  at  $0^\circ$  and then the b.p. gives  $\text{Ph}_2$  (44%),  $\text{EtOBz}$  (10%),  $\text{COPhMe}$  (41%), and (III) (6%), but no (I) or (II). *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COCl}$ ,  $\text{MgPhBr}$ , and  $\text{CoCl}_2$  (5 mol.-%) give *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$  (15%),  $\text{Ph}_2$  (70%), *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COPh}$  (33%), 2 : 2'-dimethylbenzoin, m.p.  $92^\circ$ , and  $[\cdot\text{C}(\text{C}_6\text{H}_4\text{Me}\cdot\text{o})\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{o}]_2$  (7%). Interaction occurs thus:  $\text{R}\cdot\text{COCl} + \cdot\text{CoCl} \rightarrow \text{CoCl}_2 + \text{RCO}\cdot$ ;  $\text{RCO}\cdot + \text{Et}_2\text{O} \rightarrow \text{RCO}_2\text{Et} + \text{Et}\cdot$ ;  $2\text{RCO}\cdot \rightarrow (\text{RCO})_2$ ;  $(\text{RCO})_2 + \text{MgRBr} \rightarrow \text{COR}\cdot\text{CR}_2\cdot\text{OH}$ ;  $(\text{RCO})_2 + 2\text{CoCl}\cdot \rightarrow (\cdot\text{CR}\cdot\text{OCOR})_2 \rightarrow (\cdot\text{CR}\cdot\text{O}\cdot\text{COR})_2$ .

IX.  $\text{LiPh}$  with  $\text{Bu}^a\text{Br}$  or  $\text{LiBu}^a$  with  $\text{PhBr}$  gives 52–55% of  $\text{PhBu}^a$ , the exchange,  $\text{LiPh} + \text{Bu}^a\text{Br} \rightleftharpoons \text{LiBu}^a + \text{PhBr}$ , occurring readily. In presence of 5 mol. % of  $\text{CoCl}_2$ , this exchange is largely superseded by interaction of  $\text{LiR}$  and  $\text{CoCl}_2$  to give  $\text{RCOCl}$  and thence  $\text{R}\cdot$  and  $\cdot\text{CoCl}$ . If  $R = \text{Ph}$ ,  $\text{Ph}_2$  is formed; if  $R = \text{Bu}^a$ , disproportionation to  $\text{C}_4\text{H}_{10} + \text{C}_4\text{H}_8$  occurs.  $\text{LiBu}^a\text{-PhBr}$  and  $\text{LiPh-Bu}^a\text{Br}$  with  $\text{CoCl}_2$  give 27 and 40%, respectively, of  $\text{C}_8\text{H}_{18}$ , the reaction mechanism being unknown.

X. Presence of  $\text{CoCl}_2$  (5 mol.-%) scarcely affects the products of interaction of  $\text{O}_2$  with  $\text{Mg cyclohexyl chloride}$ ,  $\text{CH}_2\text{Ph}\cdot\text{MgBr}$ , or  $\text{MgBu}^a\text{Br}$ , but with  $\text{MgPhBr}$  or *a*- $\text{C}_{10}\text{H}_7\cdot\text{MgBr}$  leads to much  $\text{Ar}_2$ . Greatly improved yields of phenols are obtained by oxidising  $\text{MgArHal}$  in presence of  $\text{MgAlkHal}$ . Reaction mechanisms are discussed.

XI. Vinyl halides do not react with Grignard reagents unless  $\text{CoCl}_2$  or  $\text{CrCl}_2$  (much less well,  $\text{CuCl}$ ) (5 mol.-%) is present. The reaction,  $\text{MgRBr} + >\text{C}:\text{CHHal} \rightarrow \cdot\text{CR}:\text{CH}_2 + \text{MgRHal}$ , occurs in moderate yield;  $\text{Ph}_2$  and polymeric hydrocarbons are also formed;  $R$  may be  $\text{Ph}$ ,  $\text{C}_{10}\text{H}_7$ , or  $\text{CH}_2\text{Ph}$ , but not *cyclohexyl* or *alkyl*; examples involve use of  $\text{CH}_2:\text{CHBr}$ ,  $\text{CH}_2:\text{CHCl}$ ,  $\text{CHMe}:\text{CHBr}$ ,  $\text{CH}_2:\text{CMeBr}$ ,  $\text{CMe}_2:\text{CMeBr}$ , and  $\text{CPh}_2:\text{CPhBr}$ .  $>\text{C}:\text{CRHal}$  do not react as above, the decomp. of  $\text{MgArHal}$  to  $\text{Ar}_2$  becoming the predominant reaction.  $\text{CPh}_2:\text{CPhBr}$  and  $\text{MgRX}$  are equilibrated by  $\text{CoCl}_2$  (0.5–1 mol.-%) with  $\text{CPh}_2:\text{CPh}\cdot\text{MgX}$  and  $\text{RBr}$ ; in presence of 2–5 mol.-% of  $\text{CoCl}_2$ ,  $\text{CPh}_2:\text{CHPh}$  and its polymerides are formed; the reaction mechanism is discussed in detail. R. S. C.

Silicon dimethyl di- and silicon methyl tri-chloride.—See B., 1943, II, 248.

Organometallic compounds of titanium, zirconium, and lanthanum. R. G. Jones (*Iowa State Coll. J. Sci.*, 1942, 17, 88–90).—Organometallic compounds could not be prepared from  $\text{Ti}$ ,  $\text{Zr}$ , and  $\text{La}$ .  $\text{TiCl}_4$  and  $\text{Ti}(\text{OEt})_4$ , but not  $\text{ZrCl}_4$ , are reduced by  $\text{LiBu}^a$ ; mol. compounds of the type  $\text{MX}_4\cdot x\text{LiR}$  were, however, observed.  $\text{TiCl}_4$ ,  $\text{Ti}(\text{OEt})_4$ , or  $\text{ZrCl}_4$  with  $\text{LiPh}$  or  $\text{MgPhBr}$  yields  $\text{Ph}_2$  but  $\text{LiMe}$  and  $\text{MgEtBr}$  give  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  respectively.  $\text{LaCl}_3$  reacts similarly but less readily. F. R. G.

## IX.—PROTEINS.

Nomographic representation of certain properties of proteins. J. Wyman, jun. and E. N. Ingalls (*J. Biol. Chem.*, 1943, 147, 297–318).—The relationships between mol. wt. and sedimentation const., diffusion const., frictional ratio, hydration, mol. shape, relaxation time, and  $\eta$  increment are represented as nomograms and their uses indicated in the cases of myoglobin, haemoglobin, and edestin. H. G. R.

Reactions of haemoglobin and its derivatives with phenylhydroxylamine and nitrobenzene.—See A., 1943, III, 454.

*Amanita* toxins. VI. Amanitin, the chief poison of *Amanita*. H. Wieland and R. Hallermayer [with W. Zilg] (*Annalen*, 1941, 548, 1–18; cf. A., 1938, II, 66; 1940, II, 233).—Improved prep. yields cryst. amanitin (I),  $\text{C}_{33}\text{H}_{45}(\text{or } 47)\text{O}_{12}\text{N}_7\text{S}$ , m.p.  $245^\circ$  (decomp.),  $[\alpha]_D^{20} +212.7^\circ$  to  $+216.8^\circ$  in  $\text{H}_2\text{O}$ ; the third substance previously reported is non-existent, impurities having greatly modified the properties of (I). 5  $\mu\text{g}$ . of (I) is fatal to mice. (I) has pH 3–3.5 in  $\text{H}_2\text{O}$ , gives a blue Hopkins-Cole reaction, reduces ammoniacal  $\text{AgNO}_3$  and I, gives a hydrolysable *K* salt and various insol. metallic salts, with  $\text{CH}_2\text{N}_2\text{-MeOH-Et}_2\text{O}$  gives methylamanitin (the *Me* ester), decomp.  $245^\circ$  (reduces  $\text{AgNO}_3\text{-aq. NH}_3$ ), and with  $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$  gives an *Ac* derivative, m.p.  $274^\circ$  (decomp.). (I) is a polypeptide,

for it gives a weak biuret and strong ninhydrin reaction, and, by hydrolysis, yields  $\text{NH}_2$ -acids. Acid hydrolysis gives  $\text{CO}_2$ . (I) probably contains a hydroxy- or thiol-indole nucleus; its absorption spectrum (max. at 251, 257, and 307  $\text{m}\mu$ .) resembles that of phalloidin. R. S. C.

Compound of methaemoglobin with thiocyanates.—See A., 1943, III, 624.

Effects of inorganic electrolytes on the liberation of  $-\text{SH}$  in proteins.—See A., 1943, I, 205.

## X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Action of nitric acid on vegetable seed shells. W. Krüger (*Ber.*, 1940, 73, [B], 493–498).—The shells of various nuts are extracted with  $\text{EtOH-C}_6\text{H}_6$  followed by  $\text{H}_2\text{O}$ , gradually added to  $\text{HNO}_3$  (*d* 1.52) at  $-10^\circ$ , and subsequently kept at room temp. for 12 hr. Undissolved matter (I) is removed and a ppt. (II) is obtained by treating the filtrate with  $\text{H}_2\text{O}$ . The yield of (I) is  $\ll$  obtained from woods and appears to diminish with increasing C content of the initial material. (I) contain 11–12% N, exclusively as nitrate. Prolonged action of  $(\text{NH}_4)_2\text{S}$  on (I) causes complete denitration but a portion of the resulting carbohydrate is dissolved; hence (I) is not a pure cellulose nitrate. The residue has the properties and elementary composition of cellulose (III) but its small amount is very significant and is best explained by Hilpert's assumption that free (III) is not present in plants. The yields of (II) vary greatly and are not related to the lignin nos., again indicating that acid lignins are not components of plant skeletons but reaction products of sensitive carbohydrates. (II) contain rather less N than (I), which is not present exclusively as nitrate, but the assumption of the presence of  $\text{NO}_2$ -compounds is not justified. The % OMe in (III) is somewhat  $>$  that of the initial materials. Similar observations are made on the action of  $\text{HNO}_3$  on lignins obtained from seed shells by  $\text{H}_2\text{SO}_4$ . The analogous behaviour of lignin preps. and sugar humins towards  $\text{HNO}_3$  shows the impossibility of regarding acid lignins as characteristic components of plants. The woody nature of plants cannot be judged by the lignin nos. The characteristic criterion of skeletal substance of plants is the OMe no. Lignification may be regarded as a high degree of methylation. H. W.

Penicillin B. Notatin.—See A., 1943, III, 686.

## XI.—ANALYSIS.

Determination of halogens in organic compounds. R. R. Umhoefer (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 383–384).—The sample is refluxed for 2.5 hr. with  $\text{Na}$  in  $\text{Pr}^b\text{OH}$  or  $\text{Bu}^b\text{OH}$ , the excess of  $\text{Na}$  destroyed with  $\text{H}_2\text{O}$ , the solution in  $\text{H}_2\text{O}$  neutralised with  $\text{HNO}_3$ , and  $\text{Cl}'$  or  $\text{Br}'$  determined titrimetrically with  $\text{AgNO}_3$  using dichlorofluorescein for  $\text{Cl}'$  or eosin for  $\text{Br}'$ . The application of the method to determination of stable F compounds is indicated. J. D. R.

Determination of fluorine in organic compounds with cerous nitrate. M. L. Nichols and J. S. Olsen (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 342–346).—The substance is decomposed with  $\text{Na}_2\text{O}_2$  in the Parr bomb, the dissolved melt neutralised, and the  $\text{F}'$  determined electrometrically with a glass electrode or visually with *Me-red* as indicator. The titration is capable of yielding results with an accuracy of 1%. The electrometric determination is superior and should be employed where the highest possible accuracy is desired. If no neutral  $\text{Na}$  salts are present, the visual titration is satisfactory and yields results equal to those obtained electrometrically.  $\text{SO}_4^{2-}$  and  $\text{ClO}_4^-$  interfere. J. D. R.

Micro-determination of arsenic in biological material.—See A., 1943, III, 704.

Micro-determination of mercury in organic compounds. H. W. Eckert (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 406–407).—The substance is refluxed at pH 7.8–8.4 with  $\text{Al}$  powder for 20 hr., and the  $\text{Al}$  dissolved in  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  followed by  $\text{NH}_2\text{OH}$ . The solution is then extracted with measured quantities of dithizone in  $\text{CCl}_4$  until 0.1 ml. of this reagent remains green. The vol. of dithizone- $\text{CCl}_4$  solution necessary is compared with the vol. needed for a standard  $\text{Hg}$  solution. J. D. R.

Apparatus for purification of hydrocarbons by recrystallisation. J. L. Keays (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 391–392).—An apparatus is described in which hydrocarbons are cryst. from  $\text{AcOH}$ , the mother-liquor withdrawn, and redistilled back to the cryst. hydrocarbon, the procedure being repeated until the m.p. is const. J. D. R.

Polarographic determination of organic peroxides. A. A. Dobrinskaja and M. B. Neiman (*Zavod. Lab.*, 1939, 8, 280–283).— $\text{H}_2\text{O}_2$ ,  $\text{MeO}_2\text{H}$ , and  $\text{Et}_2\text{O}_2$  in 0.01N- $\text{HCl}$  are reduced at 0.8, 0.6, and 0.7 v., respectively; the height of the polarographic wave is  $\propto$  the concn. of peroxide. The method is applied to analysis of the product of cold combustion of  $\text{MeCHO}$ . J. J. B.

**New reactions of  $\beta\beta'$ -dichlorodiethyl sulphide.** J. B. Polya (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 360).—Test-papers are prepared by saturating filter-paper in 2% aq.  $\text{CuSO}_4$  containing 1–2% of glycol or glycerol. On this paper,  $(\text{OH}\cdot[\text{CH}_2]_2)_2\text{S}$  (thiodiglycol) gives a green spot, most sensitive in absence of a solvent. Mustard gas (I)–HCl mixtures give a brown spot, the centre of which gradually changes to violet. A sample containing (I) is extracted with  $\text{Et}_2\text{O}$ , and the  $\text{Et}_2\text{O}$  solution refluxed with NaOH; the solution, spotted on the test-paper, gives a green colour. The test is less sensitive than the  $\text{Na}_2\text{PtCl}_6$  test. J. D. R.

**Coloured chromatograms with higher fatty acids.** M. L. Graaf and E. L. Skau (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 340–341).—The fatty acids dissolved in light petroleum are passed through a column of MgO containing 0.5% of phenol-red, and the chromatogram is developed with light petroleum. By this method it is possible to separate an unsaturated fatty acid from a saturated fatty acid with the same no. of C, and two saturated fatty acids differing in chain length by 4 C atoms. J. D. R.

**Determination of vitamin-C with the Zeiss step-photometer.**—See A., 1943, III, 667.

**Pantothenic acid. Optical rotation as a measure of stability.** D. V. Frost (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 306–310).—The destruction of pantothenate (I) under ordinary conditions can be traced to hydrolysis of the mol. and a method is described for following the destruction of Ca d(+)-pantothenate by polarimetric analysis. The rate of destruction is a function of pH and time and is affected by presence of other substances both in aq. solution and dry mixtures. The optimum stability of (I) lies in the approx. range pH 5.5–7, and the rate of destruction increases above or below this range. Only traces of  $\text{H}_2\text{O}$  are required to cause significant decomp. of (I) when other conditions favour hydrolysis. J. D. R.

**Iodometric determination of mercaptal- and mercaptol-acids.** B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1942, 15, A, No. 22, 11 pp.; cf. A., 1943, II, 119, 262).—Mercaptal- and mercaptol-acids from  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (I),  $\text{SH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , and  $\text{SH}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$  (II) are determined by fission ( $\sim 0.02\text{N}$ . solution) with  $0.022\text{N}\cdot\text{HgCl}_2$  in presence of  $0.022\text{N}\cdot\text{HCl}$  ( $\frac{1}{2}$  hr. at  $100^\circ$ ) to give, e.g.,  $\text{CMe}_2(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2 + 2\text{HgCl}_2 + \text{H}_2\text{O} \rightarrow \text{CMe}_2 + 2\text{ClHg}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + 2\text{HCl}$ , followed by addition of KI and iodometric titration. Lignin-thiolacetic acid is similarly determined in 50% AcOH, but the reaction is much slower and needs excess of  $\text{HgCl}_2$ .  $\text{CH}_2(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$  and  $\text{CO}_2\text{H}\cdot\text{CH}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$  cannot be determined owing to their very slow fission. Many alkylthiol acids (e.g.,  $\text{CHPhMe}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ) interfere by undergoing the same fission. Mercaptol acids have been prepared from (I) with  $\text{COMeEt}$ , m.p.  $112\text{--}113^\circ$ ,  $\text{COEt}_2$ , m.p.  $125\text{--}126.5^\circ$ , and  $\text{CH}_2\text{Ph}\cdot\text{COMe}$ , m.p.  $129\text{--}130^\circ$ .  $\text{SNa}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{Na}$  and  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{Br}$  in 50% EtOH, and also  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$  and (II) in  $2\text{N}\cdot\text{HCl}$ , at  $100^\circ$  give  $\beta$ -cinnamylthiolpropionic acid, m.p.  $89\text{--}90^\circ$ . M. H. M. A.

**Collection and determination of traces of formaldehyde in air.** F. H. Goldman and H. Yagoda (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 377–378).—The air is drawn at a rate of 1–3 l. per min. through 1%  $\text{NaHSO}_3$ , and the solution titrated with  $0.1\text{N}\cdot\text{I}$ , using starch, to oxidise  $\text{NaHSO}_3$  to  $\text{NaHSO}_4$ .  $\text{Na}_2\text{CO}_3\text{--NaOAc}$  is added and the  $\text{NaHSO}_3$  released from combination with  $\text{CH}_2\text{O}$  is determined titrimetrically with  $0.1\text{N}\cdot\text{I}$ . J. D. R.

**Polarographic determination of formaldehyde in biological material. Application to the determination of serine.** M. J. Boyd and K. Bambach (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 314–315).—The protein is hydrolysed with  $\text{HIO}_4$  and the  $\text{CH}_2\text{O}$  is determined in the distillate by an "electrochemograph"; the half wave of the  $\text{CH}_2\text{O}$  step occurs at  $-1.63\text{ v.}$  (normal  $\text{Hg}_2\text{Cl}_2$  electrode). Accurate temp. control ( $\pm 0.1^\circ$ ) is necessary.  $\text{MeCHO}$  formed by oxidation of protein does not interfere unless present in large amounts. J. D. R.

**Estimation of cystine by nitroprusside.** T. K. Krishnaswamy (*Proc. Indian Acad. Sci.*, 1942, 15, A, 135–138).—To 5 ml. of a solution of cystine in  $0.2\text{N}\cdot\text{HCl}$  are added with shaking 5%  $\text{NaCN}$  (2 ml.) and then 20%  $\text{Na}_2\text{SO}_3$  (1 ml.). After 1 min.  $0.5\text{N}$ . aq.  $\text{NH}_3$  (10 ml.) is added and after a further 5 min.  $0.2\text{M}\cdot\text{ZnSO}_4$  (0.2 ml.) and then 1 ml. of fresh 5% Na nitroprusside. The colour is compared with that from a standard solution (0.02%) within 5 min.  $\text{ZnSO}_4$  acts as stabiliser.  $\text{HgCl}_2$  or  $\text{CH}_2\text{O}$  suppresses the colour from disulphides and is used to detect other colour-producing substances. The method, applied to 8 protein hydrolysates, compares favourably with others. R. S. C.

**Titrimetric determination of small amounts of glucose.** F. L. Humoller (*J. Biol. Chem.*, 1943, 147, 281–290).—A cerimetric titration method involving the Müller principle of titrating to the equivalence point is described. The method gives somewhat higher blood-sugar vals. than the Folin–Wu method when  $\text{H}_2\text{WO}_4$  filtrates are used though the results agree for  $\text{Zn}(\text{OH})_2$  and  $\text{CuSO}_4\text{--Na}_2\text{WO}_4$  filtrates. Recovery of glucose added to blood is 98.5%. H. G. R.

**Identification of sulphanilamide and related drugs.** H. Minlon, C. P. Lo, and L. J. Y. Chu (*J. Chinese Chem. Soc.*, 1941, 8, 194–200).—Sulphanilamide yields  $N^4$ -acetylsulphanilamide instantaneously with  $\text{Ac}_2\text{O}$  (with or without  $\text{C}_5\text{H}_5\text{N}$ ) or slowly with boiling AcOH; boiling  $\text{Ac}_2\text{O}$  ( $1\frac{1}{2}$  hr.) or  $\text{Ac}_2\text{O}\text{--C}_5\text{H}_5\text{N}$  (1 hr.) affords  $N^1N^4$ -diacetylsulphanilamide. All  $N^1$ -substituted sulphanilamides are readily acetylated by  $\text{Ac}_2\text{O}\text{--C}_5\text{H}_5\text{N}$ . A micro-acetylation method for identifying sulphanilamides is described. Sulphanilamide derivatives having a free aromatic  $\text{NH}_2$  give deep red or orange colours with  $\text{Pb}(\text{OAc})_4$  in AcOH. A. Li.

**Amperometric titration of picrolonic acid and indirect volumetric determination of calcium by precipitation as picrolonate and back titration of the excess of picrolonic acid with methylene-blue.** G. Cohn and I. M. Kolthoff (*J. Biol. Chem.*, 1943, 148, 711–718; cf. A., 1943, I, 208).—The methods are compared with those of Bolliger (A., 1935, 1093; 1939, II, 398). Methylene-blue reduces the overvoltage of the  $\text{H}_2$  discharge at the dropping Hg electrode. Picrolonic acid is readily adsorbed from aq. solutions by filter-paper. J. E. P.

**Determination of  $p$ -aminobenzoic acid.**—See A., 1943, III, 704.

**Modified antimony trichloride reagent for determination of certain sterols and vitamin- $D_2$  and  $-D_3$ .**—See A., 1943, III, 616.

**Fluorescence reactions with boric acid and  $o$ -hydroxy-carbonyl compounds. Their application in analytical chemistry.** K. Neelakantam and L. R. Row (*Proc. Indian Acad. Sci.*, 1942, 15, A, 81–88).—Except in certain cases, adding  $\text{H}_3\text{BO}_3$  in conc.  $\text{H}_2\text{SO}_4$  to substances (in conc.  $\text{H}_2\text{SO}_4$ ) containing a phenolic OH  $o$ - to CO causes appearance or change of fluorescence in ordinary or ultra-violet light. For 9 flavones and flavonols an OH at  $\text{C}_{15}$  is needed, but increase in the no. of OH (quercetagenin, gossypetin) reduces the effect. A change is noted for naringenin, but butin does not fluoresce. Among OH-ketones (7 examples), -aldehydes (8 examples), and -acids (10 examples), and flavylum salts (3 examples), the CO  $o$ - to OH is necessary;  $\text{SO}_3\text{H}$  increases the effect, but  $\text{NO}_2$  or Br depresses it. For resacetophenone the limit of identification is 0.1 mg. and of sensitiveness 1 : 10,000; the reaction is expected to be a test for  $\text{H}_3\text{BO}_3$ . R. S. C.

**Colour reaction for natural pigments and phenols.** H. Tauber and S. Laufer (*J. Amer. Chem. Soc.*, 1943, 65, 736–737).— $\text{H}_2\text{O}_2$  in dioxan at  $34^\circ$  converts citrinin (I) into a reddish-brown substance (II), showing different colour reactions. Colours developed by (I), (II), 5 anthocyanins, 2 flavones, 2 other natural pigments, and various phenols with NaOH and  $\text{H}_2\text{O}_2\text{--NaOH}$  in aq. EtOH, before and after acidification, are listed. R. S. C.

**Differentiation of nicotinic acid and nicotinamide in the microbiological assay procedure.** L. Atkin, A. S. Schultz, W. L. Williams, and C. N. Frey (*J. Amer. Chem. Soc.*, 1943, 65, 992).—Mixtures of nicotinic acid and its amide are analysed by biological assay before and after conversion of the amide into 3-aminopyridine (inactive) by  $\text{Br}\text{--KOH}$ . R. S. C.

**Determination of nicotinamide.** C. F. Krewson (*Amer. J. Pharm.*, 1942, 115, 122–125).—The sample is hydrolysed with conc. HCl, and conc. NaOH added. The  $\text{NH}_3$  formed is determined by distillation etc. J. D. R.

**Effect of light in the Van Slyke determination of amino-groups.** H. Fraenkel-Conrat (*J. Biol. Chem.*, 1943, 148, 453–454).—Tyrosine reacts with  $\text{HNO}_2$ , producing 100–200% of the theoretical vol. of  $\text{N}_2$  depending on whether the determination is made in the dark or in strong sunlight. Phenolic compounds also yield higher vals. in the light than in the dark for their reaction with  $\text{HNO}_2$ . The method may be used to indicate the relative amounts of free phenolic groups in certain proteins and their aldehyde-treated derivatives. J. E. P.

**Determination of micro-quantities of certain proteins. Colorimetric method.** D. Pressman (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 357–359).—The protein is heated at  $100^\circ$  for 5–10 min. with NaOH, and the colour developed on addition of the Folin–Ciocalteu phenol reagent is measured photo-electrically. J. D. R.

## A., II.—Organic Chemistry

OCTOBER, 1943.

## I.—ALIPHATIC.

Application of group theory to isomerism in general.—See A., 1943, I, 220.

[Rates of] organic reactions.—See A., 1943, I, 258.

Theory of racemism. C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1239—1240).—The designation, "racemate," is definitive for substances which do not tautomerise, but is not so for tautomeric substances, for which the no. of possible racemates is the no. of tautomeric forms. Examples of the latter type are "rac."-arabinose (5 possibilities) and -perseulose. R. S. C.

Deuterohexane, m.p. 18°, from  $\alpha\beta$ -dideuterononoic acid.—See A., 1943, III, 580.

Action of sodium ethyl on (–)- $\beta$ -bromo-octane.—See A., 1943, II, 284.

Preparation of unsaturated hydrocarbons [from alcohols] by silica gel. A. Rollett and H. Maurer-Stroh (*Ber.*, 1940, **73**, [B], 740—741).— $\text{SiO}_2$  gel (I) is as good as  $\text{Al}_2\text{O}_3$  and better than clays for prep. of olefines from alcohols. Clays vary in quality, rapidly become inactivated by deposition of C, and are not fully reactivated by burning off the C.  $\text{C}_2\text{H}_4$  is formed by passing EtOH over (I) in a Cu tube at 300—550° (best 550°), fine-pored being better than coarse-pored (I). At 250° a little  $\text{Et}_2\text{O}$ , but no  $\text{C}_2\text{H}_4$ , is formed. At 450—550°,  $\text{Et}_2\text{O}$  gives nearly 100% of  $\text{C}_2\text{H}_4$ . At 450—500°  $\text{Pr}^\beta\text{OH}$  gives similarly  $\text{C}_3\text{H}_6$ .  $\text{Bu}^\beta\text{OH}$  gives a 3 : 1 and  $\text{Bu}^\alpha\text{OH}$  gives a 2 : 1 mixture of  $(\text{CHMe})_2$  and  $\text{CH}_2\text{:CHEt}$ . At 300° cyclohexanol gives  $\text{H}_2\text{O}$  and cyclohexene, and at 600° gives  $(\text{CH}_2\text{:CH})_2$  and  $\text{C}_2\text{H}_2$ . R. S. C.

Rubber, polyisoprenes, and allied compounds. IV. Relative tendencies towards substitutive and additive reaction during chlorination. G. F. Bloomfield (*J.C.S.*, 1943, 289—296).—In the chlorination of  $\text{CCl}_4$  solutions of rubber at 77° in  $\text{N}_2$ , determinations of the quantity of HCl formed and of the Cl content and I val. of the product show that the reaction is mainly substitutive during the absorption of the first  $\text{Cl}_2$ , additive and substitutive (to approx. equal extents) with the second  $\text{Cl}_2$ , and mainly substitutive with the third  $\text{Cl}_2$  per  $\text{C}_5\text{H}_8$  unit. The marked apparent loss of unsaturation, as shown by I val., during chlorination is probably due partly to cyclisation and partly to a steric effect of the substituted Cl atoms. The first stage of chlorination is accompanied by considerable decrease in  $\eta$  due (?) to autoxidation, and the products are rubber-like, but if exposed to air lose HCl and set hard. The course of the reaction is little influenced by light or change of temp., or by  $\text{O}_2$  or anti-oxidants, though these give less stable products. The above interpretation is confirmed by the fact that the products of chlorination at –30° or –80° lose no HCl when warmed to 80° in absence of air, and by the observations that chlorination (I mol.  $\text{Cl}_2$  per mol.) of 1-methylcyclohexene at 80° is 79% (calc. from HCl evolution) or 76% substitutive (calc. from I val.), while the marked differences between observed and calc. I vals. of similarly chlorinated dihydromyrcene and squalene are much diminished by reduction ( $\text{Zn} + \text{AcOH}$ ) of the products. Mono-, b.p. 88—90°/15 mm., and dichlorodihydromyrcene, b.p. 48—50°/0.01 mm., have been isolated. A. L.

Geometric isomerides of piperylene. D. Craig (*J. Amer. Chem. Soc.*, 1943, **65**, 1006—1013).—Fractional distillation of a commercial concentrate (A) yields *cis*- (I), b.p. 43.8°/750 mm., and *trans*-piperylene (II), b.p. 41.7°/745 mm. (cf. Dolliver *et al.*, A., 1937, II, 364).  $(\text{CH}\cdot\text{CO})_2\text{O}$  reacts rapidly with (II) at 100° to give 3-methyl- $\Delta^4$ -tetrahydrophthalic anhydride (nearly 100%), but only slowly with (I) to give polymeric resins (cf. Robey *et al.*, A., 1941, II, 117; Farmer *et al.*, A., 1932, 141).  $\text{SO}_2$  and (I) or more readily (II) yield 2-methyl-2 : 5-dihydrothiophen 1 : 1-dioxide (III), a  $\text{H}_2\text{O}$ -sol. oil; this difference in reaction rate permits ready prep. of pure (I); pyrolysis of (III) yields pure (II).  $\text{CuCl}\cdot\text{NH}_4\text{Cl}\cdot\text{H}_2\text{O}\cdot\text{HCl}\cdot\text{Cu}$  wool absorbs (I) or (II) to give insol. compounds, gradual thermal decomp. (60—90°) of which affords good fractionation. Mixed tetrabromides are obtained from (I) or (II) [(I) gives a relatively high yield of *threo*-tetrabromide, m.p. 114°] and with Zn regenerate mixtures of (I) and (II).  $n\text{-C}_5\text{H}_{12}$  is obtained from (I) or (II) by  $\text{H}_2$ -Raney Ni at 29—35°/~35 atm. (I) is the chain and (II) the boat form. R. S. C.

Nitration of methane.—See B., 1943, II, 271.

Production of magnesium alkoxides.—See B., 1943, II, 272.

Optically active  $\alpha\gamma$ -dimethylallyl alcohols. M. P. Balfe, H. W. J. Hills, J. Kenyon, H. Phillips, and B. C. Platt (*J.C.S.*, 1943, 348—351; cf. A., 1936, 820).—(+) and (–) refer to the sign of rotatory power of optically pure substances and *d*- and *l*- to substances of unspecified optical purity. (+)- $\text{CHMe}\cdot\text{CH}\cdot\text{CHMe}\cdot\text{OH}$  (I) is converted by  $\text{SOCl}_2$  or (better)  $\text{PCl}_3\text{-C}_5\text{H}_5\text{N}$  into *l*- $\alpha\gamma$ -dimethylallyl chloride (II), which gives largely racemised products with MeOH or  $\text{Bu}^\alpha\text{OH}$  probably because these reactions are initiated by ionisation of (II) and with solid KOAc or AgOAc possibly due to the heterogeneous reaction conditions. In homogeneous medium (II) and NaOMe give a highly racemised product, suggesting that the unimol. (ionisation) mechanism controls even the homogeneous replacement. Hydrolysis of (I) by  $\text{H}_2\text{O}$  gives a *laevo*-alcohol (III) similar in magnitude of rotatory power to the (+)-alcohol. By methods which produce optically active derivatives from (+)- or (–)-alcohol (III) gives an optically inactive H phthalate and methyldibromo-*n*-propylcarbinol; it does not therefore contain the normal form of (–)- $\alpha\gamma$ -dimethylallyl alcohol. (III) is convertible into an acetate,  $\alpha_{\text{D}}^{20} -0.66^\circ$  ( $l = 1$ ), and a  $\text{CHMePr}^\alpha\cdot\text{OH}$ ,  $[\alpha]_{\text{D}}^{18} +0.3^\circ$  ( $l = 1$ ), these vals. being ~2% of those of the corresponding derivatives of (I). It appears that the major product of the hydrolysis of (II) is *dl*- $\text{CHMe}\cdot\text{CH}\cdot\text{CHMe}\cdot\text{OH}$  but that an optically active impurity of unknown nature is present. A *laevorotatory* substance appears also to be formed during the mutarotation of (I) since the change, though erratic, leads to a fall in  $[\alpha]$  with ultimate change in sign; a specimen having  $\alpha_{\text{D}}^{20} +0.70^\circ$ ,  $\alpha_{\text{D}}^{70} -2.66^\circ$  after 48 hr. at 70° had  $\alpha_{\text{D}}^{70} -3.22^\circ$  and, after cooling,  $\alpha_{\text{D}}^{20} +0.47^\circ$  ( $l = 1$ ) and the alcohol recovered from the action of (I) and PhNCO is *laevorotatory* but from (I) which has become *laevorotatory* during mutarotation the recovered alcohol is also *laevorotatory*. The H phthalate obtained from the alcohol at various stages of its mutarotation diminishes (by >10%) in rotatory power but this change is much less marked than that of the parent alcohol and the sign of rotation of the phthalate is always the same even when that of the alcohol from which it is obtained is reversed. A survey of the literature suggests that the mutarotation of the unsymmetrically substituted allyl alcohols is due to anionotropic rearrangement with concomitant racemisation but this explanation cannot be applied to (I). H. W.

Stereoisomerism of unsaturated compounds. VI. Composition of divinylglycol from acraldehyde. System *meso-dl*-diethylglycol. W. G. Young, S. J. Cristol, and F. T. Weiss (*J. Amer. Chem. Soc.*, 1943, **65**, 1245—1246; cf. A., 1939, II, 399).—Hydrogenation ( $\text{PtO}_2$ ; 95% EtOH) of  $(\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{OH})_2$  [obtained by reduction of  $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$  (I)] gives a mixture [whence *meso*- (II) and *dl*- $(\text{CHEt}\cdot\text{OH})_2$  are isolated] which is shown by thermal analysis [eutectic contains 21.5% of (II)] to be 52 : 48 mixture. The same mixture is obtained if (I) was mixed with  $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ . R. S. C.

Volatile borates of polyhydric alcohols and the activation of boric acid. R. E. Rippere and V. K. La Mer (*J. Physical Chem.*, 1943, **47**, 204—234).—Interaction of  $\text{H}_3\text{BO}_3$  with polyhydric alcohols has been investigated by determining the amount of liberated  $\text{H}_2\text{O}$ . Ethylene, propylene, trimethylene,  $\beta\gamma$ -,  $\alpha\gamma$ -, and *iso*-butylene glycol form borates,  $\text{R}\langle\text{O}\rangle\text{B}\cdot\text{OH}$ . The boiling ranges at 1 mm. or less are 176—187°, 110—114°, 147—151° (3 mm.), 112—117°, 107—109°, and 76—79° respectively. A compound with glycerol is formed but could not be isolated. Glycerol  $\text{Et}_1$  and  $\text{Bu}_1$  ethers and glycerol chlorohydrin form compounds of the same general type, the boiling ranges at <1 mm. being 145—150°, 162—165°, and 160—165° (decomp.) respectively. Three mols. of  $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{OMe}$  combine with 1 mol. of  $\text{H}_3\text{BO}_3$  or  $\text{HBO}_2$  to a compound of the same type as  $\text{Me}_3\text{BO}_3$  with a boiling range 91—99° at <1 mm. Propylene and ethylene glycols "activate"  $\text{H}_3\text{BO}_3$  in titrations in presence of  $\text{H}_2\text{O}$ , although not to the same extent as mannitol. C. R. H.

Reactions of ethers with chromous halides. F. Hein and H. Kraft (*J. pr. Chem.*, 1940, [ii], **154**, 285—308).— $\text{CrCl}_2$  or  $\text{CrBr}_2$  and dioxan in  $\text{N}_2$  give fission products which cannot be isolated; treating the reaction product with  $\text{NH}_3$  gives *ppts.*, which after washing with  $\text{Et}_2\text{O}$ , have sometimes the composition,  $3\text{NH}_3\cdot\text{CrHal}_2\cdot\text{O}\cdot[\text{CH}_2]_2\cdot\text{O}\cdot\text{CrHal}_2\cdot 3\text{NH}_3$  containing indefinite amounts

of  $\text{Et}_2\text{O} + \text{NH}_3$  of solvation (cf. A., 1930, 1019). However, the ppts. are often solvated mixtures thereof with  $\text{Cr}(\text{O}[\text{CH}_2]_2\text{O})_3\text{Cr}$ . Treatment with  $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$  (I) gives similar mixed ppts. in which 1 mol. of (I) replaces each  $3\text{NH}_3$ . The double fission is proved by formation of  $(\text{CH}_2\text{OH})_2$  as sole alcohol (only  $\text{H}_2\text{C}_2\text{O}_4$  formed by oxidation with  $\text{HNO}_3$ ) when the  $\text{NH}_3$  adduct is heated in  $\text{H}_2\text{O}$ .  $\text{CH}_2\text{Ph}\cdot\text{OEt}$  similarly gives products,  $\text{CrHal}_2\cdot\text{OEt}\cdot 3\text{NH}_3$ ,  $+x\text{Et}_2\text{O}$ , and mixtures thereof with  $\text{Cr}(\text{OEt})_3$ .  $\text{MeOH}$  at  $-50^\circ$  to  $-60^\circ$  gives products,  $\text{CrHal}_2\cdot\text{OMe}\cdot 3\text{NH}_3$ ,  $+x\text{Et}_2\text{O}$ .  $(\text{CH}_2\text{Ph})_2\text{O}$  reacts to give, presumably,  $\text{CrHal}_2\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ , but the ppt. produced by  $\text{NH}_3$  is difficult to analyse. Aryl alkyl and diaryl ethers and cineole do not react with  $\text{CrHal}_2$ . Methylfurfuraldehyde and furfuraldehyde react but the products were not investigated. The fate of the second fragment of the ethers is unknown. The ppts. formed by  $\text{NH}_3$  are all amorphous. The first portions are greenish, the later portions reddish-violet. At  $-50^\circ$  to  $-60^\circ$  a liquid phase is formed containing the product in liquid  $\text{NH}_3 + \text{ROR}'$ ; warming removes the  $\text{NH}_3$  (and  $\text{Me}_2\text{O}$ ); washing with  $\text{Et}_2\text{O}$  then give products similar in composition to those above but resinous and almost black. Fresh ppts. immediately give  $\text{AgHal}$  from  $\text{AgNO}_3$ , indicating their structure as  $[\text{Cr}\cdot\text{OR}\cdot 5\text{NH}_3]\text{Hal}_2 + m\text{ROR}' + n\text{NH}_3$ ; the  $\text{NH}_3$  of solvation is detectable by odour. Keeping over  $\text{H}_2\text{SO}_4$  in vac. removes first the "excess" of  $\text{NH}_3$  (giving odourless products) and then the ability to give ionisable  $\text{Cl}$ , which is interpreted as gradual conversion into  $[\text{CrHal}_2\cdot\text{OR}\cdot 3\text{NH}_3] + m\text{ROR}'$ ; these products are odourless. Warming the products in  $\text{H}_2\text{O}$  causes the colour to change through violet-red and dark red to dark green, giving finally gels owing to hydrolysis to  $\text{CrCl}(\text{OH})_2$ . Keeping the products, particularly solvated  $3\text{NH}_3\cdot\text{CrCl}_2\cdot\text{O}[\text{CH}_2]_2\cdot\text{O}\cdot\text{CrCl}_2\cdot 3\text{NH}_3$ , in  $\text{MeOH}$  causes alcoholysis to  $\text{Cr}(\text{OMe})_3$ .  $\text{EtOH}$  causes slower formation of  $\text{Cr}(\text{OEt})_3$ .  
R. S. C.

**Mercaptan syntheses with thioacetic acid.** B. Sjöberg (*Ber.*, 1941, 74, [B], 64—72; cf. A., 1939, I, 86).—Epichlorohydrin and  $\text{AcSH}$  at  $60^\circ$  (I uptake min. after 12 hr.) give 75%  $\alpha$ -acetyl-,  $\text{SAC}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$  (I), b.p.  $94^\circ/0.4$  mm., which, on further heating at  $60^\circ$  or on prolonged interaction of the starting materials, is partly converted into  $\beta$ -acetyl-thiochlorohydrin,  $\text{SH}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\text{Cl}$  (II), b.p.  $69\text{—}70^\circ/1$  mm., which, in contrast to (I), consumes I; (I) is converted into (II) to the extent of 80% at room temp. in 14 days.  $\alpha\gamma$ -Dichlorohydrin acetate (III), b.p.  $76^\circ/12$  mm., and  $\text{AcSK}$  in  $\text{EtOH}$  at  $60^\circ$  give: (i) unchanged (III), (ii)  $\alpha\beta$ -diacetylthiochlorohydrin (IV), b.p.  $105\text{—}110^\circ/1.7$  mm.,  $95^\circ/0.9$  mm., and (iii)  $\alpha\beta\gamma$ -triacetyl- $\alpha\gamma$ -dithioglycerol, b.p.  $135\text{—}140^\circ/1.7$  mm. (I) and  $\text{AcCl}$  give (IV), b.p.  $102\text{—}103^\circ/1$  mm. (I), (II), and (IV), on trans-esterification ( $\text{MeOH}$ —1%  $\text{HCl}$ ), afford thiochlorohydrin (V), b.p.  $57^\circ/1.3$  mm. ( $\text{CMe}_2$  derivative, b.p.  $74\text{—}75^\circ/15$  mm.); the three specimens of (V) show identical unimol. decomp. coeffs. in aq. alkali.  $\text{AcSH}$  and  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$  at  $60^\circ$  give 79% of  $\alpha$ -acetyl- $\gamma$ -chloropropyl mercaptan, b.p.  $83\text{—}84^\circ/10$  mm., which, with  $\text{MeOH}$ — $\text{HCl}$ , affords 81% of  $\gamma$ -chloropropyl mercaptan, b.p.  $52^\circ/12$  mm.,  $145.5^\circ/760$  mm., also obtained from  $\text{Br}\cdot[\text{CH}_2]_3\cdot\text{Cl}$  and  $\text{KSH}$ .  
J. WA.

**Preparation of allyl and methylallyl methylacrylates by thermal decomposition of allyl and methylallyl  $\alpha$ -acetoxisobutyrate.** C. E. Rehberg, C. H. Fisher, and L. T. Smith (*J. Amer. Chem. Soc.*, 1943, 65, 1003—1006).—Allyl (64.5%), b.p.  $73^\circ/20$  mm., and  $\beta$ -methylallyl  $\alpha$ -hydroxyisobutyrate (70%), b.p.  $78^\circ/16$  mm., are obtained by boiling the acid (1 mol.), alcohol (3 mols.), and a little  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  in  $\text{C}_6\text{H}_6$  with continuous removal of  $\text{H}_2\text{O}$ . With  $\text{Ac}_2\text{O}$  at  $80\text{—}100^\circ$  and then  $100\text{—}110^\circ$  these give the  $\alpha$ -acetoxisobutyrate, b.p.  $96^\circ/19$  mm., and  $106^\circ/19$  mm., respectively, pyrolysis of which, best at  $475\text{—}500^\circ$ , yields 70—75% of allyl, b.p.  $67^\circ/50$  mm., and  $\beta$ -methylallyl  $\beta$ -methylacrylate, b.p.  $63^\circ/17$  mm. Pyrolysis is thus readier than that of the lactates (A., 1943, II, 251). Allyl and  $\beta$ -methylallyl  $\alpha$ -OH-esters are more stable than the Bu or  $\text{OPh}\cdot[\text{CH}_2]_2$ , less stable than the Me, Et, or  $\text{CH}_2\text{Ph}$ , and as stable as the  $\text{OMe}\cdot[\text{CH}_2]_2$ , esters.  
R. S. C.

**Vitamin-E. XLII. Long-chain compounds with recurring "isoprene" units.** L. I. Smith and G. F. Rouault (*J. Amer. Chem. Soc.*, 1943, 65, 745—750).—Methods of introducing isoprene units into aliphatic chains and of converting unsaturated alcohols into the next lower acid are described. Slow distillation of perhydrogeranyl palmitate (prep. from citronellol by  $\text{H}_2$ -catalyst and then  $\text{RCOCl}$  at  $150^\circ$ ) at  $310^\circ$  gives 27% of  $\text{Pr}^\beta\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2$  (I), b.p.  $152^\circ/740$  mm., and much unchanged ester, but that of the stearate at  $360^\circ$  gives 84% of (I).  $\text{KMnO}_4$  converts (I) in  $\text{COMe}_2$ — $\text{NaHCO}_3$  at  $7^\circ$  into  $\alpha\epsilon$ -dimethyl-n-heptoic acid (45%), b.p.  $115^\circ/3$  mm. (*S*-benzylthiuronium salt, m.p.  $141\text{—}143.5^\circ$ ). Adding the crude derived ( $\text{PCl}_5$ ) chloride (decomposes when distilled) to *p*-cresol and  $\text{AlCl}_3$  at  $145^\circ$  gives 3- $\alpha\epsilon$ -dimethyl-n-heptoyl-*p*-cresol (69%), b.p.  $144^\circ/3$  mm., which, with  $\text{H}_2$ —Raney Ni at  $195^\circ/1700\text{—}3700$  lb. (in  $\text{EtOH}$ ) and then  $175^\circ/1700\text{—}2400$  lb. (no  $\text{EtOH}$ ), gives 4-methyl-2- $\beta\zeta$ -dimethyl-n-heptylcyclohexanol (96%), b.p.  $133^\circ/3$  mm. (dinitrophenylurethane, an oil), dehydrated by a little  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  (II) (not  $\text{H}_3\text{PO}_4$ ) to 5-methyl-1- $\beta\zeta$ -dimethyl-n-heptyl- $\Delta^1$ -cyclohexene (87%), b.p.  $141^\circ/15$  mm. 6%  $\text{O}_3$  in  $\text{EtBr}$  and then 30%  $\text{H}_2\text{O}_2$  ( $\text{H}_2\text{O}_2$  alone gives a poor yield) in  $\text{AcOH}$  converts this into  $\epsilon$ -keto- $\gamma\eta\lambda$ -trimethyl-n-tridecoic acid

(92%), b.p.  $170^\circ/4$  mm. With  $\text{Zn}$ — $\text{Hg}$  and  $\text{EtOH}$ — $\text{HCl}$  this affords *Et*  $\gamma\eta\lambda$ -trimethyl-n-tridecoate, b.p.  $160^\circ/3$  mm., which with  $\text{H}_2$ —Cu chromite at  $250^\circ/2800$  lb. gives  $\delta\mu$ -trimethyl-n-tridecanol (85%), b.p.  $140^\circ/3$  mm., converted by gaseous  $\text{HBr}$  at  $120^\circ$  into the bromide ( $\approx 57\%$ ), b.p.  $135^\circ/2\text{—}3$  mm., the Grignard reagent from which with  $\text{MeCHO}$  yields  $\zeta\kappa\zeta$ -trimethyl-n-pentadecan- $\beta$ -ol, oxidised by  $\text{Na}_2\text{Cr}_2\text{O}_7$ — $\text{H}_2\text{O}$ — $\text{AcOH}$ — $\text{H}_2\text{SO}_4$  to "phytol ketone" (95%). 3-Dodecyl-*p*-cresol, m.p.  $43\text{—}45^\circ$ , b.p.  $190^\circ/3$  mm., with  $\text{H}_2$ —Raney Ni in  $\text{EtOH}$  at, successively,  $150^\circ$ ,  $165^\circ$ ,  $185^\circ$ , and  $200^\circ$  (all at  $1700\text{—}2800$  lb.) yields 4-methyl-2-n-dodecylcyclohexanol (III) (78%), f.p.  $\sim 28^\circ$ , b.p.  $178^\circ/2$  mm., but in absence of a solvent at  $175^\circ/2200$  lb. and then (fresh catalyst)  $225^\circ$  gives 1-methyl-3-n-dodecylcyclohexane (55%), b.p.  $148^\circ/2$  mm. With  $\text{Na}_2\text{Cr}_2\text{O}_7$ — $\text{H}_2\text{SO}_4$ — $\text{H}_2\text{O}$ — $\text{AcOH}$ , (III) gives 4-methyl-2-n-dodecylcyclohexanone (86%), b.p.  $170\text{—}171^\circ/3$  mm. (semicarbazone, m.p.  $86\text{—}89^\circ$ ; 2:4-dinitrophenylhydrazone, m.p.  $68\text{—}72^\circ$ ), and with (II) at  $180^\circ$  gives 5-methyl-1-n-dodecyl- $\Delta^1$ -cyclohexene (74%);  $\text{KHSO}_4$  at  $320^\circ$  gives 60%;  $\text{H}_3\text{PO}_4$  gives none, b.p.  $190^\circ/3$  mm. This yields, as above (not by  $\text{KMnO}_4$ ),  $\epsilon$ -keto- $\gamma$ -methylstearic acid (93%), b.p.  $190^\circ/3$  mm., and thence *Et*  $\gamma$ -methylstearate, b.p.  $175^\circ/3$  mm., and  $\delta$ -methyl-n-octadecan- $\alpha$ -ol (58%), b.p.  $170^\circ/3$  mm.  $\text{Pr}^\beta\text{COCl}$  gives only 25% of 3:1:4- $\text{Pr}^\beta\text{CO}\cdot\text{C}_6\text{H}_5\text{Me}\cdot\text{OH}$ .  
R. S. C.

**sec.-Butyl stearate, linolenate, b.p.  $193\text{—}195^\circ/0.01$  mm., and oleate, b.p.  $163\text{—}165^\circ/0.01$  mm.**—See A., 1943, III, 670.

**Enol ether-acetal equilibrium in the ethyl acetoacetate series.** F. Arndt, L. Loewe, and M. Ozansoy [with A. Gönenç and Z. Lugal] (*Ber.*, 1940, 73, [B], 779—782).—Heating 1 mol. of  $\text{AcCl}$  with  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  and  $\text{CH}(\text{OEt})_3$  gives  $\text{OMe}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$  (I), m.p.  $31^\circ$ , but use of 0.1 mol. of  $\text{AcCl}$  gives  $\sim 4$  parts of (I) and 1 part of  $(\text{OEt})_2\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  (II) (cf. Claisen, A., 1894, i, 66; 1896, i, 463; 1898, i, 421). (I) or nearly pure (II) is converted by 2—4 mols. of  $\text{NaOEt}$  in cold or hot  $\text{EtOH}$  into a 3:1 mixture of (I) and (II), proving presence of an equilibrium favouring (I).  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  and  $\text{OEt}\cdot\text{CH}\cdot\text{NH}_2\cdot\text{HCl}$ ,  $\text{HgCl}_2$  in  $\text{EtOH}$  at  $0^\circ$  and then room temp. give a mixture, whence removal of (I) by fractional freezing at  $-20^\circ$  gives 80—90% pure (II); this boils at  $81\text{—}83^\circ/6$  mm. or  $68\text{—}69^\circ/2$  mm., but at 760 mm. gives (I) +  $\text{EtOH}$ .  
R. S. C.

**Identification of ascorbic acid.**—See A., 1943, III, 667.

**Autoxidation of ascorbic acid.**—See A., 1943, I, 259.

**Preparation of substituted malonic esters.**—See B., 1943, II, 273.

**Synthesis of  $\alpha$ -bromoadipic acid.** J. von Braun and F. Meyer (*Ber.*, 1941, 74, [B], 19—21).— $\text{Br}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{Et}$  with  $\text{CHNa}(\text{CO}_2\text{Et})_2$  in  $\text{Et}_2\text{O}$  gives 61% of  $\text{CH}(\text{CO}_2\text{Et})_2\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{Et}$  (I), b.p.  $172\text{—}174^\circ/13$  mm., and a small fraction, b.p.  $200\text{—}204^\circ/13$  mm., probably  $\text{C}(\text{CO}_2\text{Et})_2\cdot([\text{CH}_2]_3\cdot\text{CO}_2\text{Et})_2$ . (I) and  $\text{Br}$  react readily giving *Et*<sub>3</sub>  $\alpha$ -bromobutane- $\alpha\alpha\delta$ -tricarboxylate, b.p.  $186^\circ/12$  mm., which when carefully hydrolysed with fuming  $\text{HBr}$  gives the (impure) free bromotricarboxylic acid, m.p.  $135\text{—}148^\circ$ , passing on short heating at  $\geq 145^\circ$ , with loss of  $\text{CO}_2$ , into  $\alpha$ -bromoadipic acid (70%), m.p.  $126^\circ$  (*Et*<sub>2</sub> ester, b.p.  $138^\circ/0.6$  mm.).  
J. WA.

**Action of diazomethane on mannosaccharic acid.** O. T. Schmidt and H. Kraft (*Ber.*, 1941, 74, [B], 33—49; cf. A., 1938, II, 42).—Mannosaccharic acid (I), m.p.  $128^\circ$  (obtained pure from the amide via the K and Ag salts), with dry and then moist  $\text{CH}_2\text{N}_2$  gives a substance ( $\text{OMe}$ , 39.2, 39.02%), b.p.  $138\text{—}142^\circ/0.15$  mm.,  $[\alpha]_D^{20} -28.1^\circ$  in  $\text{MeOH}$ . Similarly, mannosaccharodilactone (II) affords  $\alpha\delta$ -dimethylmannosaccharodilactone (III), m.p.  $143^\circ$ ,  $[\alpha]_D^{20} +249^\circ$  ( $\pm 2.5^\circ$ )  $\rightarrow -44^\circ$  ( $\pm 2.2^\circ$ ) after 12 months (in  $\text{H}_2\text{O}$ ) (diphenylhydrazide, m.p.  $183\text{—}186^\circ$ ,  $[\alpha]_D^{20} -57.54^\circ$  in  $\text{MeOH}$ ), stable to Fehling's solution but consuming 0.2 I per mol.; more I is consumed as  $\text{NaOI}$ , giving  $\text{CHI}_3$ . (III) and aq.  $\text{NH}_3$  give  $\alpha\delta$ -dimethylmannosaccharodiamide (IV), m.p.  $183\text{—}185^\circ$  (decomp.),  $[\alpha]_D^{20} -55.39^\circ$  ( $\pm 0.5^\circ$ ) (hemihydrate in  $\text{H}_2\text{O}$ ). Attempts to prepare the free acid from (IV) via Na and Ag salts give (III). (IV) with  $\text{NaOCl}$  followed by  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$  gives no  $(\text{NH}_2\cdot\text{CO}\cdot\text{NH})_2$  (V), whereas the diamide of (I) under the same conditions gives 72% of (V). Anhyd. (II) with 10—11 mols. of  $\text{CH}_2\text{N}_2$  gives *Me*<sub>2</sub>  $\alpha\alpha'$ -dimethoxymuconate (cis-trans form) (VI), m.p.  $139\text{—}140^\circ$  [also obtained from (III) with  $\text{CH}_2\text{N}_2$ ], reduced ( $\text{H}_2$ — $\text{PtO}_2$  in  $\text{EtOAc}$ ) to a mixture of liquid racemic and meso- (VII)-forms of *Me*<sub>2</sub>  $\alpha\alpha'$ -dimethoxyadipate. (VII), m.p.  $53^\circ$ , is also obtained by methylating meso- $\alpha\alpha'$ -dihydroxyadipic acid with  $\text{CH}_2\text{N}_2$  followed by  $\text{MeI}$ — $\text{Ag}_2\text{O}$ .  $\alpha\alpha'$ -Dimethoxymuconic acid (cis-trans), m.p.  $196\text{—}197^\circ$ , obtained from (VI) by alkaline hydrolysis, passes when heated with  $\text{H}_2\text{O}$  into 3-methoxy-2-pyrone-6-carboxylic acid (Me ester, m.p.  $215^\circ$ ), m.p.  $261^\circ$  (decomp., sinters  $234^\circ$ ). In one case the methylation product of (II) is distilled in a poor vac. and *Me*<sub>2</sub>  $\alpha\alpha'$ -dimethoxymuconate (cis-cis form?) (VIIa), m.p.  $63\text{—}64^\circ$ , b.p.  $130\text{—}150^\circ/3\text{—}5$  mm. (free acid, m.p.  $169\text{—}171^\circ$ ), is obtained, passing on hydrogenation into (VII) and its *dl*-form. (VIIa) decomposes on keeping to give *Me*<sub>2</sub>  $\alpha\alpha'$ -diketodihydromuconate (?), m.p.  $120\text{—}121^\circ$ , and on irradiation in  $\text{C}_6\text{H}_6$  in presence of I is converted into an isomeride (trans-trans form?) (VIIb), m.p.  $115\text{—}116^\circ$ , identical with the product from  $\text{CH}_2\text{N}_2$  and  $\alpha\alpha'$ -dihydroxymuconic acid, m.p.  $226\text{—}227^\circ$ .  
J. WA.

**Preparation of D-galacturonic acid from pectin.** E. Rietz and W. D. Maclay (*J. Amer. Chem. Soc.*, 1943, **65**, 1242—1243).—74—80% yields are obtained by use of Pectinol 46 AP. R. S. C.

**Hydrogenolysis of sulphur compounds by Raney nickel catalyst.** R. Mozingo, D. E. Wolf, S. A. Harris, and K. Folkers (*J. Amer. Chem. Soc.*, 1943, **65**, 1013—1016).—Relatively large amounts of Raney Ni containing absorbed  $H_2$ , but without added  $H_2$ , convert aliphatic or aromatic  $RR'S$ ,  $RS'SR'$ ,  $RR'SO$ , or  $RR'SO_2$  in, e.g., boiling EtOH or MeOH into  $RH$ ,  $R'H$ , and (?) Ni sulphides. Thus,  $S([CH_2]_4 \cdot CO_2H)_2$  (2.5 g.) and Raney Ni (25—30 g.) in boiling 75% EtOH give 94% of  $Bu^aCO_2H$ ;  $\gamma$ -methylthiol-n-butyric acid, b.p. 143—144°/16 mm., gives  $Pr^aCO_2H$ ;  $l-(-)-[S \cdot CH_2 \cdot CH(NHBz) \cdot CO_2H]_2$  gives  $l-(+)-NHBz \cdot CHMe \cdot CO_2H$ ,  $[\alpha]_D^{25} + 9.7^\circ$  in EtOH, thus correlating the configurations;  $dl-SMe \cdot [CH_2]_2 \cdot CH(NHBz) \cdot CO_2H$  gives  $NHBz \cdot CHEt \cdot CO_2H$ , and the derived *hydantoin*, m.p. 109—110°, behaves similarly;  $p-C_6H_4Me \cdot SH$ ,  $(p-C_6H_4Me \cdot S)_2$ , or  $(CH_2Ph)_2S$  gives  $PhMe$ ;  $Ph_2S$ ,  $Ph_2SO$ , and  $Ph_2SO_2$  give  $C_6H_6$ . R. S. C.

**Catalytic preparation of cyclic acetals of aldehydes and ketones.** G. Willfang (*Ber.*, 1941, **74**, [B], 145—153; cf. A., 1938, II, 2).—CO-compounds, except hydroxy-carbonyl compounds such as aldol, with epichloro- and epibromo-hydrin in  $CCl_4$  in presence of  $SnCl_4$  (best),  $AlCl_3$ ,  $FeCl_3$ , or  $SbCl_5$  give cyclic acetals. The reaction is not particularly sensitive to moisture and, after the catalyst is destroyed with alkali or an org. base, the products are readily purified by distillation. *Acetaldehyde*, 45% yield, b.p. 158—162°/760 mm., *crotonaldehyde*, 75%, b.p. 68—70°/1.5 mm., *cyclopentadecanone*, b.p. 100—120°/0.003—0.006 mm., m.p.  $\sim 33^\circ$ , *camphor*, 83%, b.p. 114—122°/1.85 mm., *bromoacetophenone*, 65.3%, b.p. 133°/1.5 mm., and *benzophenone*  $\gamma$ -chloropropylene acetal, 71%, b.p. 159—167°/2—3 mm., m.p. 44.5°, and *chloral*, 54%, b.p. 94—100°/14—15 mm., and *Et\_2 ketone*  $\gamma$ -bromopropylene acetal, 68.5%, b.p. 82—85°/2 mm., are described. The halogen atoms in the above compounds are very inert towards  $C_5H_5N$ , KI, anhyd.  $NaOAc$ ,  $AgNO_3$ , Mg, and NaOH. J. W.A.

**Determination of paracetaldehyde.**—See B., 1943, II, 269.

**Reduction of chloral by organometallic compounds.  $\alpha\alpha\alpha$ -Trichlorobutan- $\beta$ -ol.** H. Gilman and R. K. Abbott, jun. (*J. Org. Chem.*, 1943, **8**, 224—229).—In the reaction between  $CCl_3 \cdot CHO$  and  $MgEtHal$  there is no significant production of  $CCl_3 \cdot CH_2 \cdot OH$  (I), the main product being  $CCl_3 \cdot CH_2 \cdot OH$  formed by reduction. (I) does not appear to be formed from  $CCl_3 \cdot CHO$  and  $PbEt_4$ .  $CCl_3 \cdot CHO$  and  $CH_2N_2$  afford trichloropropylene oxide (II), b.p. 39—40°/11 mm., transformed by  $MgMeI$  in  $Et_2O$  into  $\alpha\alpha\alpha$ -trichloro- $\gamma$ -iodopropan- $\beta$ -ol, m.p. 54—55°. With  $LiMe$  in  $Et_2O$  at  $-75^\circ$  (II) gives (I), b.p. 169—171°/738 mm. (*p*-nitrobenzoate, m.p. 70—71.5°), hydrolysed by  $Na_2CO_3$  in boiling aq. EtOH to  $OH \cdot CH_2 \cdot CO_2H$ . In the Lucas test (I) passes into  $\alpha\alpha\alpha$ -tetrachloro-n-butane, b.p. 134—135°/742 mm.  $CCl_3 \cdot CHO$  and  $CH_2Ph \cdot MgCl$  afford  $CCl_3 \cdot CH_2 \cdot OH$  in small amount. H. W.

**Catalytic degradation of heptaldehyde in the vapour phase.** T. J. Suen and S. Fan (*J. Amer. Chem. Soc.*, 1943, **65**, 1243—1245).—Passing  $n-C_6H_{13} \cdot CHO$  (I) over Ni at 250° in absence of  $H_2$  (cf. A., 1942, I, 233; apparatus modified) gives liquids [43—67%;  $n-C_6H_{14}$  (II) including 1.9—15% of unchanged (I) and 24—30% of  $C_6H_{12}$ ], CO 48.2—57.4,  $H_2O$  12.0—18.9,  $CH_4$  13.1—14.4,  $O_2$  1.6—5.4,  $CO_2$  0.4—1.4, unsaturated gases 0.6—1.8, and  $N_2$  (by difference) 11.1—19.9%. Absence of  $H_2$  causes rapid depreciation of the Ni. The  $C_6H_{12}$  is probably the  $\Delta\beta$ -isomeride (b.p.;  $n$ ); it is probably the primary product, giving (II) by interaction with the  $H_2$  formed. A considerable part of the (I) is completely converted into gases. Reaction is incomplete at 200°;  $\sim 35\%$  of the liquid product is then  $C_6H_{12}$ . R. S. C.

**Catalytic conversion of ethyl alcohol into acetone.**—See B., 1943, II, 269.

**Production of amines.**—See B., 1943, II, 273.

**Compounds of gallium.**—See A., 1943, I, 233.

**Stovaine analogues.** W. T. Olson and F. M. Whitacre (*J. Amer. Chem. Soc.*, 1943, **65**, 1019—1020).—Passing  $CH_2Cl \cdot CH_2 \cdot OH$  (prep. by adding  $Bu^aI$  to  $KOH \cdot EtOH$  at  $\sim 90^\circ$ ) into aq.  $HOCl$  gives  $CH_2Cl \cdot CH_2 \cdot OH$ , b.p. 53—55°/17 mm., which with  $NH_2Et$  in  $C_6H_6$  at 120° yields  $NEt_2 \cdot CH_2 \cdot CH_2 \cdot OH$ , b.p. 74—75°/22 mm. [benzoate, b.p. 120—122° (corr.)/2 mm. (hydrochloride; picrate, m.p. 112°). *iso*Butylene oxide,  $NH_2Et$ , and a little  $H_2O$  at 105—110° give  $NEt_2 \cdot CH_2 \cdot CMe_2 \cdot OH$ , b.p. 65—68°/23—25 mm. (picrate, m.p. 99.2—100.2°; benzoate hydrochloride, m.p. 149.5—150°).  $NH_2 \cdot CH_2 \cdot CH_2 \cdot OH$  and  $EtBr$  in boiling aq.  $Na_2CO_3$  give  $NEt_2 \cdot CH_2 \cdot CH_2 \cdot OH$  (I), b.p. 86—87°/25 mm. [hydrochloride, an oil; benzoate, b.p. 124—126° (corr.)/2 mm. (hydrochloride); picrate, m.p. 113—114°]. Anaesthetic action of the above benzoate hydrochlorides (prep. by  $BzCl$  in boiling  $C_6H_6$ ) and those of stovaine,  $NEt_2 \cdot CH_2 \cdot CMe_2 \cdot OH$ , and  $NMe_2 \cdot CH_2 \cdot CMe_2 \cdot OH$  are recorded; (I) is comparable with novocaine. Ethylation of  $NH_2 \cdot CMe_2 \cdot CH_2 \cdot OH$  gives only  $NH_2Et \cdot CMe_2 \cdot CH_2 \cdot OH$ , m.p. 74.5—75° (picrate, m.p. 124.7—125.3°; hydrochloride, m.p. 136.5°). M.p. are corr. R. S. C.

**Reaction of formaldehyde with  $l-(+)$ -aspartic and -glutamic acids.** D. C. Carpenter and F. E. Lovelace (*J. Amer. Chem. Soc.*, 1943, **65**, 1161—1165).—Measurement of  $[\alpha]$  and  $[H]$  during interaction of  $CH_2O$  with  $l-(+)$ -aspartic and -glutamic acids shows 1:1 (mol.) interaction, followed by interaction with a second mol. of  $CH_2O$  to give unstable compounds. Equilibrium consts. are calc. The initial products are  $OH \cdot CH_2$  compounds (cf. A., 1943, II, 122). R. S. C.

*p*-Toluenesulphonyl-aspartic acid, m.p. 159—160° (anhydride, m.p. 158.5—160°; benzyl esters, m.p. 135.5—137° and 108.5—109°), -asparagine, m.p. 174.5—175.5°, and -isoasparagine, m.p. 177.5—178°.—See A., 1943, III, 604.

**New type of complex silver compounds with trivalent silver.**—See A., 1943, I, 260.

## II.—SUGARS AND GLUCOSIDES.

**Effect of boric acid on the caramelisation of sugars.** M. Niculescu (*Z. anal. Chem.*, 1941, **122**, 335—344).—Data showing the inhibiting effect of  $H_3BO_3$  on the caramelisation of solutions of glucose, lactose, sucrose, and milk are discussed. The effect is attributed to combination between  $H_3BO_3$  and the sugar. L. S. T.

**Action of diazomethane on acyclic sugar derivatives. IV. Ketose synthesis.** M. L. Wolfrom, R. L. Brown, and E. F. Evans (*J. Amer. Chem. Soc.*, 1943, **65**, 1021—1027; cf. A., 1943, II, 57).—*D*-Arabonic acid tetra-acetate and  $PCl_5$  in  $Et_2O$  give *D*-arabonyl chloride tetra-acetate (85%), m.p. 74—75°,  $[\alpha]_D^{25} + 46^\circ$  (cf. A., 1942, II, 395). Adding  $KHCO_3$  and then Br to crude aldehydo-*D*-galactose penta-acetate (modified prep.) in  $H_2O$  at 25° gives *D*-galactonic acid penta-acetate (44%), m.p. 127—130°,  $[\alpha]_D + 16.5^\circ$ , converted, as above, into the chloride penta-acetate (I) (90—92%), m.p. 80—81°,  $[\alpha]_D^{21} + 3^\circ$  [gives the known amide and the Et ester penta-acetate, m.p. 110—111°,  $[\alpha]_D^{27} + 9.5^\circ$  (cf. Kohn, A., 1895, i, 504)], which with  $CH_2N_2$  in  $Et_2O$  at 0° gives 1-diazo-1-deoxyketo-*D*-galactose penta-acetate, pale yellow, m.p. 136—137°,  $[\alpha]_D^{23} + 64^\circ$  (const.). This evolves  $N_2$  slowly in  $H_2O$  at room temp., more rapidly if heated or in presence of  $Cu^{++}$ ,  $Ag^+$ , or acids, and reduces aq.  $AgNO_3$  or halogens. With  $NH_3 \cdot MeOH$  at 0—5° it gives 1-diazo-1-deoxy-*D*-galactose (71%), m.p. 140° (decomp.),  $[\alpha]_D^{23} + 82^\circ$  in  $H_2O \rightarrow$  (at 0°)  $+ 93^\circ$ , unstable in  $H_2O$  at room temp. or, more so, in aq.  $HCO_2H$ , and in boiling AcOH yields keto-*D*-galactose hexa-acetate, forms, m.p. 100—102° and 116—117°,  $[\alpha]_D^{23-27} - 1.6^\circ$  in  $CHCl_3$ ,  $-20^\circ$  in  $C_6H_6$  (different X-ray diagrams), which is the enantiomorph of keto-*L*-perseulose hexa-acetate (Khouvine *et al.*, A., 1938, II, 219) and with aq.  $Ba(OH)_2$  at 0—5° gives *D*-galactose [D-perseulose; *D*-gala-*L*-fructoheptose] (55%),  $+ 0.5H_2O$ , m.p. 101—102° (102—103° after drying),  $[\alpha]_D^{25} + 90.6^\circ \rightarrow + 75.3^\circ$  in  $H_2O$  (with *L*- gives *dl*-perseulose, m.p. 136—137°). *D*-Glucoheptulose, softens 168°, m.p. 171—173°,  $[\alpha]_D^{18} + 67^\circ$  (const.) in  $H_2O$ , is obtained from its hexa-acetate in 77% yield by  $Ba(OH)_2$  at 0—5°.  $NHPh \cdot NH_2$  and (I) in  $Et_2O$  give *D*-galactonophenylhydrazide penta-acetate, m.p. 136.5—137°,  $[\alpha]_D^{21} + 36^\circ$ , converted by  $ZnCl_2 \cdot Ac_2O$  at 0° and then room temp. into *D*-galactonacetphenylhydrazide penta-acetate, m.p. 218°,  $[\alpha]_D^{29} + 23^\circ$ , which is also obtained from *D*-galactonophenylhydrazide by  $Ac_2O \cdot C_5H_5N$  at room temp. (cf. Robbins *et al.*, A., 1940, II, 266). *D*-Gluconyl chloride penta-acetate yields similarly glucono-phenylhydrazide penta-acetate, m.p. (anhyd.) 127.5—128.5° (128—128.5°) and ( $+H_2O$ ) 86—88°,  $[\alpha]_D^{22} + 37.0^\circ$  in  $CHCl_3$ ,  $[\alpha]_D^{21} + 17.5^\circ$  in EtOH, and -acetphenylhydrazide penta-acetate, m.p. 152—153°,  $[\alpha]_D^{22} + 33^\circ$  in  $CHCl_3$ ,  $+ 25^\circ$  in EtOH (cf. Major *et al.*, A., 1937, II, 49). Unless otherwise stated,  $[\alpha]$  are in  $CHCl_3$ . R. S. C.

**Glucosidation of 2:3:6-trimethylglucose.** K. Freudenberg and W. Jakob (*Ber.*, 1941, **74**, [B], 162—163; cf. A., 1943, II, 255).—The small amount of dimethylglucose isolated from methylated starch (I) owes its origin to demethylation of trimethylglucose under the conditions used for methanolysis, or hydrolysis of (I) and glucosidation. The following are very mild conditions. 2:3:6-Trimethylglucose affords 94% of the methylglucoside when treated with  $Si(OMe)_4$ , MeOH, and HCl at 80°, or 95% at 20° when HCl is replaced by  $AcCl$ .  $CH(OMe)_3$  can replace  $Si(OMe)_4$ . J. W.A.

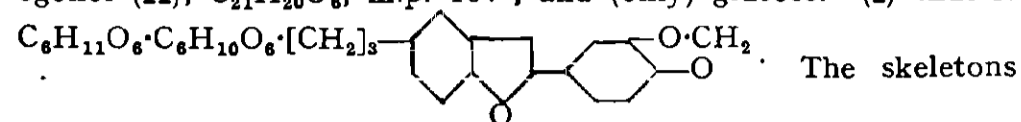
**Constitution of 1-phenyl-*d*-fructosone.** H. Ohle and M. Hielscher (*Ber.*, 1941, **74**, [B], 18—19).—1-Phenyl-*d*-fructosone (I) was known to react with only 1 mol. of  $NHPh \cdot NH_2$  and the possibility of a mol. rearrangement in its prep. had to be considered. However, (I) with  $o-C_6H_4(NH_2)_2$  in boiling EtOH gives 2-phenyl-3-*d*-arabo-tetra-hydroxybutylquinoxaline (II), m.p. 198°,  $[\alpha]_D^{20} - 145^\circ$  in aq.  $C_5H_5N$  (1:1). (II) with 3 mols. of  $NHPh \cdot NH_2$  in boiling  $H_2O$  and  $H_2$  gives much unchanged (II) and 2-phenylquinoxaline-3-aldehyde phenylhydrazide, m.p. 176°, which shows the anticipated colour reactions. J. W.A.

**Vitamin-P.**—See A., 1943, III, 579.

**Mechanism of polysaccharide production from sucrose.** S. Hestrin and S. Avineri-Shapiro (*Nature*, 1943, **152**, 49—50).—Levan sucrase shows optimal activity at pH 5.5; its solutions are stable at 0° but are inactivated by boiling. Production of levan from raffinose is not regarded as proceeding by way of intermediately

formed sucrose. It ceases when levan concn. is 300—500 mg.-%; increase in initial sucrose concn. beyond a necessary min. does not shift the position of the levan end-point. Known poisons of respiration or glycolysis do not retard levan production. A. A. E.

**Egonol. XII.** Egonol glucoside from the fruits of "Taiwan-Egonoki." S. Kawai and K. Sugimoto (*Ber.*, 1940, 73, [B], 774—776; cf. A., 1943, II, 275).—This plant is *Styrax formosanum*, Matsum. (cf. A., 1939, II, 32). It yields *egonol diglucoside* (I),  $C_{31}H_{38}O_{15}$ , +2H<sub>2</sub>O (lost at 110°/12 mm.), m.p. 143° (decomp.),  $[\alpha]_D^{25}$  (anhyd.) -29.8° in AcOH, which in boiling 10% H<sub>2</sub>SO<sub>4</sub> gives egonol (II),  $C_{21}H_{26}O_6$ , m.p. 107°, and (only) glucose. (I) thus is



of lignans and (II) are formed from 2 C<sub>6</sub>-C<sub>3</sub> and C<sub>6</sub>-C<sub>3</sub> + C<sub>6</sub>-C<sub>2</sub> units, respectively. R. S. C.

**Molecular constitution of amylose and amylopectin of potato starch.** W. Z. Hassid and R. M. McCready (*J. Amer. Chem. Soc.*, 1943, 65, 1157—1161).—Potato starch contains ~20% of amylose (I),  $[\alpha]_D +155^\circ$  in N-NaOH. Methylation and end-group analysis indicate 300—400 glucopyranose units per mol. of (I) but only 25 units for amylopectin (II),  $[\alpha]_D +161^\circ$  in N-NaOH. Hydrolysis of (II) by  $\beta$ -amylase is stopped at 54% conversion (i.e., 13—15 units) by side-chains. R. S. C.

**Separation and determination of amylose and amylopectin in potato starch.** R. M. McCready and W. Z. Hassid (*J. Amer. Chem. Soc.*, 1943, 65, 1154—1157).—When potato starch is treated with H<sub>2</sub>O at 60—70°, the granules swell but do not burst. Centrifuging the filtered solution separates amylopectin (I). MeOH then ppts. amylose (II), which is insol. in H<sub>2</sub>O, completely hydrolysed by  $\beta$ -amylase, and gives a brilliant blue colour with I, is identical with the amyloamylose of Samec and Mayer (A., 1921, i, 707), and resembles synthetic starch. 60—64% of whole starch is hydrolysed by  $\beta$ -amylase. The amounts of (I) and (II) in mixtures of starch are determined colorimetrically by I-KI. R. S. C.

**Constitution of starch.** E. Bois (*Canad. Chem.*, 1943, 27, 362, 364).—The unit of the starch mol. is a pentahexose (I) of which successive pairs of hexoses (overlapping) represent gentiobiose, cellobiose, maltose, and sucrose; this is associated with a second similar but oppositely oriented (I), giving a decahexose (II) with OH groups blocked by oxonium linkings. Amylose comprises four (II) units in a closed ring, whereas amylopectin is composed of chains of (II) associated with P. I. A. P.

**Structural difference of starches differentiated colorimetrically by iodine.** M. Samec (*Ber.*, 1940, 73, [A], 85—92).—A lecture summarising the differences between amylose (blue I colour) and amylopectin (red I colour) in their mol. wt., behaviour on dialysis, pptn. by EtOH and tannin, adsorption on cotton, effect on H<sub>2</sub>O<sub>2</sub>, oxidation by KMnO<sub>4</sub>, and hydrolysis by acid and enzymes. The P content has no significance. A pictorial representation of the enzyme attack is given. R. S. C.

**Dextrins from maize starch.**—See A., 1943, III, 682.

**Determination of carbonyl groups in chromic anhydride oxystarch and oxycellulose by means of hydroxylamine.** E. K. Gladding and C. B. Purves (*Paper Trade J.*, 1943, 116, TAPPI Sect., 150—155).—The reaction  $>C=O + NH_2OH \cdot HCl = >C=N \cdot OH + H_2O + HCl$  is followed by titration of the liberated HCl with standard alkali. The highly buffered nature of the system renders the method unsuitable for technical oxycelluloses although massive amounts of  $>CO$  are determined with an accuracy of ~5%. Simple sugars condense in first-order reactions which are complete within either 1.5 or 18 hr. at 20° and the  $>CO$  groups are classified as fast or slow. All CHO in periodate oxycellulose (I) or oxystarch are fast although the reactions are not of the first order. When unswollen linters is oxidised with increasing amounts of CrO<sub>3</sub> in AcOH at 20° up to 28% of the oxidant is accounted for as CO<sub>2</sub>H and "fast" CO in the insol. (I) and H<sub>2</sub>O-sol. products result even with relatively small amounts of oxidant. Unswollen, powdered starch is not appreciably affected under the same conditions. With highly swollen linters duplicate oxidations proceed very much more rapidly and cause no perceptible production of H<sub>2</sub>O-sol. material until an oxidation level of ~0.3 atom of O per glucose unit is reached. ~75% of the O consumed below this level is represented by insol. (I) but the recovery falls sharply thereafter. The fate of the remaining 25% is not elucidated though it may have produced slow CO groups in (I). The chemical course of oxidations which are not accompanied by substantial swelling may be dominated by the extent of the colloidal surface present in the original material. The colloidal condition of the latter is not nearly so crit. when the CrO<sub>3</sub> is dissolved in 0.2N-H<sub>2</sub>SO<sub>4</sub>, probably because aq. solutions exert a powerful swelling action. H. W.

**Action of nitric acid on vegetable seed shells.**—See A., 1943, II, 286.

### III.—HOMOCYCLIC.

**Halogenation of cyclohexane.**—See B., 1943, II, 274.

**Catalytic hydrogenation of benzene over metal catalysts.**—See A., 1943, I, 260.

**Number of structural isomerides in simple ring compounds. I.** T. L. Hill (*J. Physical Chem.*, 1943, 47, 253—260).—Mathematical. General functions for determining the no. of possible structural isomerides in substituted symmetrical ring compounds have been derived. C. R. H.

**Determination of benzene. Detection and estimation of benzene in presence of toluene, xylene, and other substances.**—See B., 1943, II, 269.

**Photometric determination of benzene, toluene, and their nitro-derivatives.**—See B., 1943, II, 270.

**Organic reactions with boron fluoride. XXVI. Friedel-Crafts type alkylations with boron trifluoride.** G. F. Hennion and R. A. Kurtz (*J. Amer. Chem. Soc.*, 1943, 65, 1001—1003; cf. A., 1942, II, 84).—*tert.*-Alkyl halides and CH<sub>2</sub>PhCl readily alkylate C<sub>6</sub>H<sub>6</sub> in presence of BF<sub>3</sub> if H<sub>2</sub>O or the appropriate alcohol is also present; *sec.*-alkyl halides give low yields, raised somewhat by adding also H<sub>2</sub>SO<sub>4</sub> (and H<sub>2</sub>O); *n*-alkyl halides do not react. Small amounts of *p*-dialkylation sometimes occur. The lower reaction layer can be re-used, particularly if re-saturated with BF<sub>3</sub>. R. S. C.

**Colorimetric determination of alkylbenzenesulphonates.**—See B., 1943, II, 270.

**Ethylenic stereoisomerism. VI. Crystalline *cis*-stilbene.** C. Weygand and I. Rettberg (*Ber.*, 1940, 73, [B], 771—773).—Various old samples of *cis*-(CHPh)<sub>2</sub> (I), prepared from (CPh)<sub>2</sub>, contained (CPh)<sub>2</sub>, (CH<sub>2</sub>Ph)<sub>2</sub>, and/or *trans*-(CHPh)<sub>2</sub> (II), since they yield in AcOH the adducts thereof with *s*-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub> (III), m.p. 155° (lit. 96°; ? dimorphism), 102°, and —, respectively. The final filtrate is freed from (III) by chrysene; the residual (I) is fractionated; a colourless distillate, b.p. 93°/0.08 mm., crystallised (m.p. 1°) when scratched; a yellow distillate crystallised when seeded. When freshly prepared from CHPh·CPh·CO<sub>2</sub>H and freed from (II) by (III), (I) crystallised spontaneously. R. S. C.

**Tribenzylsulphonium hydrogen sulphate and hydroxide.** O. Haas and G. Dougherty (*J. Amer. Chem. Soc.*, 1943, 65, 1238—1239).—In conc. H<sub>2</sub>SO<sub>4</sub> at 70—80° (CH<sub>2</sub>Ph)<sub>2</sub>S (I) gives (CH<sub>2</sub>Ph)<sub>3</sub>S·HSO<sub>4</sub>, m.p. 171°, and thence *tribenzylsulphonium hydroxide*, m.p. 133° [when heated, gives (I) and CH<sub>2</sub>Ph·OH], and the additive compound, (CH<sub>2</sub>Ph)<sub>3</sub>SI, HgI<sub>2</sub>, m.p. 137—138°; the nitrate is an oil. R. S. C.

**Absorption of light by  $\alpha\epsilon$ -dien- $\gamma$ -inenes.**—See A., 1943, I, 217.

**Conversion of 2:7-dibromofluorene into 2:7-dibromophenanthrene.** W. G. Brown and B. A. Bluestein (*J. Amer. Chem. Soc.*, 1943, 65, 1235—1236).—2:7-Dibromo-9-formylfluorene, m.p. 171° (acetate, m.p. 219°), is obtained in 85% yield by boiling 2:7-dibromofluorene in KOEt-Et<sub>2</sub>O and then adding HCO<sub>2</sub>Et. It is reduced by Al(OPr<sup>i</sup>)<sub>3</sub>-Pr<sup>i</sup>OH to 2:7-dibromo-9-fluorenylcarbinol (58%), m.p. 154° (acetate, m.p. 190°), which with P<sub>2</sub>O<sub>5</sub> in boiling xylene gives 2:7-dibromophenanthrene, m.p. 207° (lit. 202°, quinone, m.p. 321° (lit. 323°)) (cf. A., 1941, II, 247). R. S. C.

**Dehydrogenation. III. Dehydrogenation of a methylspiran.** M. Levitz and M. T. Bogert (*J. Org. Chem.*, 1943, 8, 253—255).—1:1-Pentamethylene-1:2:3:4-tetrahydronaphthalene (Perlman *et al.*, A., 1937, II, 11) is oxidised by CrO<sub>3</sub> in AcOH to 4-keto-1:1-pentamethylene-1:2:3:4-tetrahydronaphthalene, b.p. 140—142°/3 mm. [*semicarbazone*, m.p. 204.5—205.5° (corr.)]. This is converted by MgMeI into the corresponding carbinol, which is dehydrated by KHSO<sub>4</sub> at 150—160°/18 mm. to 1:1-pentamethylene-4-methyl-1:2-dihydronaphthalene, b.p. 109—110°/2 mm. This is dehydrogenated (Pd-C at 330°) to 9-methylphenanthrene, m.p. 90—91° (corr.) [picrate, m.p. 156° (corr.)]. There is no shift in the initial position of Me (cf. Marvel *et al.*, A., 1941, II, 15). H. W.

**Arylnaphthacene series. III.** A. Weizmann (*J. Org. Chem.*, 1943, 8, 285—289; cf. A., 1939, II, 548).—Me<sub>2</sub> benzylsuccinate, b.p. 125—135°/1.5 mm., is converted by PhCHO and Na powder in Et<sub>2</sub>O followed by hydrolysis into benzylbenzylidenesuccinic acid, m.p. 160—162°, which is hydrogenated (Pd-BaSO<sub>4</sub> in boiling Pr<sup>i</sup>OH or Pr<sup>i</sup>OH) to a mixture of *s*-dibenzylsuccinic acids, transformed by conc. H<sub>2</sub>SO<sub>4</sub> at 100° into 5:11-diketo-5:5a:6:11:11a:12-hexahydronaphthacene (I), m.p. 220—222°. With LiPh in Et<sub>2</sub>O under N<sub>2</sub> at room temp. (I) affords the *peroxide*, C<sub>24</sub>H<sub>18</sub>O<sub>3</sub>, m.p. 295—298°, and with 1:3:6-Li·C<sub>6</sub>H<sub>3</sub>Br·OMe it gives (?) 5-keto-6:11-di-(5'-bromo-2'-methoxyphenyl)-5:5a:6:11:11a:12-hexahydronaphthacene, m.p. 278°, which is resistant towards boiling AcCl. With Li·C<sub>6</sub>H<sub>4</sub>Me-*p* (I) yields 5:11-di-*p*-tolyl-naphthacene, m.p. 335—336°. H. W.

**1:2:3:4-Dibenzphenanthrene and its derivatives. I. Synthesis with chrysene as starting material.** F. Bergmann and H. E. Eschinazi (*J. Amer. Chem. Soc.*, 1943, 65, 1413—1417).—Chrysene,

AcCl, and AlCl<sub>3</sub> in CS<sub>2</sub> at room temp.—60° give 2- (I), m.p. 145°, and some (? 4-)acetyl- (II), m.p. 254°, and x : y-diacetyl-chrysene, m.p. 296° (cf. Funke *et al.*, A., 1936, 472). MgMel (3 mols.) and (I) in Et<sub>2</sub>O, later boiling xylene, give 2-*α*-hydroxyisopropyl- (III) (60%), m.p. 172°, and 2-isopropenyl-chrysene (IV) (25%), m.p. 161°, b.p. 220°/2 mm. [picrate, m.p. 144°, also obtained from (III)]. Adding conc. H<sub>2</sub>SO<sub>4</sub> to (III) in cold AcOH gives (IV), but at 100° a dimeride, m.p. 307°, is obtained. (II) gives similarly (? 4-)isopropenylchrysene, m.p. 288°. MgEtBr and (II) give β-2-chrysenyl-Δ<sup>8</sup>-n-butene (V) (68%), m.p. 159—160° [inert towards (:CH·CO)<sub>2</sub>O (VI); picrate (VII), m.p. 132—133°], and β-2-chrysenyl-n-butan-β-ol (26%), m.p. 119° [gives (VII)]. MgPr<sup>+</sup>Br or MgBu<sup>+</sup>Br gives similarly β-2-chrysenyl-Δ<sup>8</sup>-n-pentene (67%), m.p. 102° (picrate, m.p. 138—140°), and -n-hexene, m.p. ~40° (picrate, m.p. 129—130°), respectively. H<sub>2</sub>-Pd-BaSO<sub>4</sub> reduces (IV) or (slowly) (V) in EtOAc to 2-isopropyl-, m.p. 137° (picrate, m.p. 144—145°), and 2-sec-butyl-chrysene, m.p. 100° (picrate, m.p. 133°), respectively, but the higher homologues are unaffected. In boiling Ac<sub>2</sub>O, (III) or, less well, (IV) with (VI) gives 4-methyl-1 : 2 : 3 : 11-tetrahydro- (VIII) (80%), dimorphic, m.p. 262°, dehydrogenated by Pb(OAc)<sub>4</sub> in boiling AcOH to 4-methyl- (20%); Br-NaOAc-AcOH gives 30% of impure product (IX), m.p. 325°, 2' : 1'-9 : 10-naphthophenanthrene-1 : 2-dicarboxylic anhydride. Distilling (VIII) with Zn at 100 mm. gives (IV), but heating with Se at 270—310° gives 4'-methyl-1' : 2' : 3' : 4'-tetrahydro-1 : 2-benz-chrysene (X) (50%), m.p. 139° (picrate, m.p. 140°; 7 : 8-quinone, m.p. 178°), which with Se at 310—320° yields a small amount of a substance (picrate, m.p. 165°). Heating (IX) with basic Cu carbonate in quinoline gives 4-methyl-2' : 1'-9 : 10-naphthophenanthrene-1- or -2-carboxylic acid, m.p. 292—293°. Carcinogenic activity is affected by alkyl side-chains in so far as they simulate, sterically, active rings. R. S. C.

**Benzcyclooctatetraenes. III. Diphenylene and tetraphenylene.** W. S. Rapson, R. G. Shuttleworth, and (in part) J. N. van Niekerk (*J.C.S.*, 1943, 326—327).—The Grignard reagent from 2 : 2'-(C<sub>6</sub>H<sub>4</sub>Br)<sub>2</sub> with CuCl<sub>2</sub> in Et<sub>2</sub>O yields diphenylene and 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-tetrabenz-Δ<sup>1:3:5:7</sup>-cyclooctatetraene, m.p. 233° [Br- (Br and a trace of Fe in CCl<sub>4</sub>), m.p. 182°, and (NO<sub>2</sub>)<sub>4</sub>-derivative (HNO<sub>3</sub>, d 1.5, +H<sub>2</sub>SO<sub>4</sub> on the CCl<sub>4</sub> solution), m.p. 195—197°], which is unaffected by KMnO<sub>4</sub> in boiling COMe<sub>2</sub>, and forms no additive compounds with picric or styphnic acid or C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>. Crystallographic data confirm the constitution. A. Li.

**Perylene and its derivatives. LII.** A. Zinke and H. Troger [in part with E. Posch]. **LIII. Synthesis of 2 : 3 : 10 : 11-dibenzoperylene.** A. Zinke and E. Ziegler (*Ber.*, 1941, 74, [B], 107—115, 115—118).—LII. Perylene (I) with Br vapour or with Br in C<sub>6</sub>H<sub>6</sub> gives an unstable compound, C<sub>20</sub>H<sub>10</sub>Br<sub>4</sub>, readily passing with loss of Br into a mixture of 3 : 9- (II), m.p. 287°, and 3 : 10-dibromoperylene (III), m.p. 221°. (III) with conc. H<sub>2</sub>SO<sub>4</sub>, then H<sub>2</sub>O, gives 3 : 10-perylenequinone. (II) and (III) with Br vapour give unstable Br<sub>2</sub>-derivatives which decompose on keeping, heating to 140—150°, or treatment with KI, with regeneration of (II) and (III). 3 : 9-Dibenzoylperylene readily absorbs ~8 Br. The unstable dark additive compound readily loses Br to give 3 : 9-dibromo-4 : 10-dibenzoylperylene, m.p. 355°, converted by KOH in boiling NH<sub>2</sub>Ph or quinoline into isoviolanthrone. The amount of I taken up by (I) depends on concn. in C<sub>6</sub>H<sub>6</sub>. 3 : 9-Dinitro- and 3 : 9-dicyanoperylene do not react with Br and 3 : 9-dichloroperylene reacts only in solution with Br and not with the vapour.

LIII. 9 : 9'-Diphenanthryl, m.p. 188—189°, from 9-bromophenanthrene and Cu powder at 330—350°, with AlCl<sub>3</sub>-NaCl at 120—130° gives 2 : 3 : 10 : 11-dibenzoperylene (IV) [1 (or 4) : 12 (or 9)-quinone, m.p. 330° (darkening)], m.p. 343—345° (sinters at 327°) and 299—300° in admixture with the supposed (IV) of Brass *et al.* (A., 1939, II, 207). J. WA.

**Synthesis of physiologically active amines. Amines derived from phenyl styryl ketones.** J. Algar, A. Hickey, and P. G. Sherry (*Proc. Roy. Irish Acad.*, 1943, 49, B, 109—119).—Ph *α*-chloro-β-amino-β-phenylethyl ketone hydrochloride, m.p. 195°, is prepared from COPh·CHBr·CHPhBr (I) by EtOH-NH<sub>3</sub> followed by EtOH-HCl. Ph *α*-chloro-β-methylamino-β-phenylethyl ketone hydrochloride, m.p. 169°, similarly prepared from (I) and aq. NH<sub>2</sub>Me, yields Ph β-methylamino-β-phenylethyl ketone hydrochloride, m.p. 191°, with Pt-H<sub>2</sub>-H<sub>2</sub>O. Ph *α*-chloro-β-methylamino-β-p-anisyl-, m.p. 170°, and -β-3 : 4-methylenedioxyphenyl-ethyl ketone hydrochloride, m.p. 174°, are similarly prepared. Reduction (H<sub>2</sub>, Pt, EtOH-HCl) of COPh·C(N·OH)·CH<sub>2</sub>Ph gives β-amino-*α*-diphenyl-n-propyl alcohol hydrochloride (II), m.p. 250° (decomp.) (free amine, m.p. 115°). β-Amino-*α*-phenyl-γ-3 : 4-methylenedioxyphenyl-n-propyl alcohol, m.p. 142° [hydrochloride (III), m.p. 197° (decomp.)], is similarly obtained. Ph 3 : 4-methylenedioxy-styryl ketone oxide, m.p. 96°, yields an oxime (poor yield), m.p. 169°, which could not be reduced by Pt-H<sub>2</sub> or Na-Hg and EtOH. COPh·CH<sub>2</sub>·NMe<sub>3</sub>Cl (+H<sub>2</sub>O), new m.p. 204° (decomp.), is obtained from the oxides of Ph styryl or *p*-methoxystyryl ketone and EtOH-NMe<sub>3</sub>. In general only the compounds having NH<sub>2</sub> *α* to CO or OH [(II) and (III)] have marked physiological action and cause a reduction in blood pressure. J. H. BA.

**Synthesis of 4 : 5-trimethyleneisoquinoline etc.**—See A., 1943, II, 278.

**Monoreduction of dinitronaphthalenes in acid solution and of 1 : 5- and 1 : 6-dinitronaphthalene by aqueous sodium sulphide.** H. H. Hodgson and H. S. Turner (*J.C.S.*, 1943, 318—319).—Reduction of 1 : 6-C<sub>10</sub>H<sub>6</sub>(NO<sub>2</sub>)<sub>2</sub> with SnCl<sub>2</sub> in AcOH-HCl yields 6 : 1-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·NH<sub>2</sub> whilst aq. EtOH-Na<sub>2</sub>S gives 5 : 2-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·NH<sub>2</sub>. 1 : 3-C<sub>10</sub>H<sub>6</sub>(NO<sub>2</sub>)<sub>2</sub> with SnCl<sub>2</sub> gives 3 : 1- and 4 : 2-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·NH<sub>2</sub>. 1 : 5-C<sub>10</sub>H<sub>6</sub>(NO<sub>2</sub>)<sub>2</sub> with Na<sub>2</sub>S gives 5 : 1-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·NH<sub>2</sub>, whilst 1 : 5- and 1 : 8-C<sub>10</sub>H<sub>6</sub>(NO<sub>2</sub>)<sub>2</sub> with SnCl<sub>2</sub> (excess or deficit) afford the C<sub>10</sub>H<sub>6</sub>(NH<sub>2</sub>)<sub>2</sub>. J. H. BA.

**New reaction of sulphanilamide.** W. T. Somerville (*J. Chem. Educ.*, 1943, 20, 238).—Sulphanilamide gives a bright orange coloration with substances containing lignin (I). The reaction detects the presence of (I) in paper, wood, and various vegetable fibres. Manila hemp (no reaction) can be easily distinguished from sisal fibres by this reaction, which is better than that for (I) with aniline sulphate. L. S. T.

**Preparation of phenols.**—See B., 1943, II, 275.

**Separation of individual cresols and xylenols from their mixtures.**—See B., 1943, II, 270.

**Stimulation of formation of additive compounds between bases and phenol derivatives by lipid solvent.**—See A., 1943, I, 259.

**Preparation of pentabromophenol and bromanil from phenol.** M. Kohn (*J. Chem. Educ.*, 1943, 20, 117).—Working details are given. L. S. T.

**Halogeno-*p*-tert.-octylphenols.**—See B., 1943, II, 275.

**Long-chain compounds with recurring "isoprene" units.**—See A., 1943, II, 291.

**Formation of phenols by ozonisation of benzene derivatives. II.** E. Späth, M. Pailer, and G. Gergely (*Ber.*, 1940, 73, [B], 795—804; cf. A., 1943, II, 227).—Phenols, as well as acids and aldehydes, are often obtained when substituted CHPh:CHR (R usually = CO<sub>2</sub>Me) or PhCHO are treated with O<sub>3</sub> (1.5 mols.) in CHCl<sub>3</sub> at 0° and the product is boiled with Zn dust and a little AgNO<sub>3</sub> in H<sub>2</sub>O. The OH replaces the CH:CHR or CHO. OAlk, probably best *o*- or *p*-, or other accelerating substituents must be present, but general rules cannot be laid down. The following are yields of phenol, acid, and aldehyde, respectively, from CHPh:CH·CO<sub>2</sub>Me, having the named substituents: 2 : 4 : 5-(OMe)<sub>3</sub> 48.2, 2.4, 7.8; 3 : 4-(OMe)<sub>2</sub>-6-Et 46.4, 5.1, 11.5; 2 : 4-(OMe)<sub>2</sub>-6-Me 27.1, trace, 72.0; 4-OMe-2 : 5-Me<sub>2</sub> 22.0, 5.2, 61.7; 6-OMe-3 : 4-Me<sub>2</sub> 15.9, 15.0, 54.0; 2 : 4-(OMe)<sub>2</sub> 15.0, 2.2, 28.8; 2 : 3 : 4-(OMe)<sub>3</sub> 13.7, 17.1, 45.6; 3 : 4-(OMe)<sub>2</sub> trace, 22.3, 59.0; 5-Br-3 : 4-(OMe)<sub>2</sub> trace, 15.0, 83.5%; *p*-Me and 4 : *α*-Me<sub>2</sub> trace, —, —. *iso*Apiol give 5.0, 2.3, and 54.3%, respectively. (CHPh)<sub>2</sub> gives no PhOH. Yields of phenol and acid, respectively, from substituted PhCHO are: 2 : 3 : 4- 20.1, 43.0, and 2 : 4 : 5-(OMe)<sub>3</sub> 4.1, 3.1; 3 : 4-(OMe)<sub>2</sub>-6-Et 14.5, 21.0; 2 : 4-(OMe)<sub>2</sub> 14.0, 39.1; 2 : 4-(OMe)<sub>2</sub>-6-Me 8.0, 11.6; 4-OMe-2 : 5-Me<sub>2</sub> 4.4, 14.5; 6-OMe-3 : 4-Me<sub>2</sub> 3.9, 18.0; 5-Br-3 : 4-(OMe)<sub>2</sub> trace, 15.1%. 6-Methoxy-3 : 4-dimethylbenzaldehyde (prep. from 6 : 3 : 4 : 1-OH·C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·CHO by Me<sub>2</sub>SO<sub>4</sub>-KOH-MeOH), m.p. 66°, with CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> and piperidine at 100° gives 6-methoxy-3 : 4-dimethylcinnamic acid, m.p. 168° (Me ester, m.p. 64—66°). Similarly are prepared 4-methoxy-2 : 5-dimethyl-, m.p. 205° (lit. 200—202°) (Me ester, m.p. 81°), 2 : 4-dimethoxy-6-methyl-, m.p. 190° (Me ester, m.p. 101°), 2 : 3 : 4-trimethoxy-, m.p. 173° (lit. 172°) (Me ester, m.p. 55°), and 5-bromo-3 : 4-dimethoxy-cinnamic acid, m.p. 142° (Me ester, m.p. 78°). The following are also described: 6 : 3 : 4 : 1-, m.p. 146° (lit. 142.5—143.5°), and 4 : 2 : 5 : 1-OMe·C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·CO<sub>2</sub>H, m.p. 168° (lit. 163—165°); 5-methoxy-*o*-4-xyleneol, m.p. 69—70°; 3 : 5-dimethoxy-*o*-cresol, m.p. 107°; 2 : 4 : 6 : 1-(OMe)<sub>4</sub>·C<sub>6</sub>H<sub>2</sub>Me·CHO, m.p. 62°; 2 : 3 : 4 : 1-(OMe)<sub>4</sub>·C<sub>6</sub>H<sub>2</sub>·CO<sub>2</sub>H, m.p. 100—102° (lit. 99°, 100°); 2 : 4 : 1-(OMe)<sub>3</sub>·C<sub>6</sub>H<sub>3</sub>·OH, m.p. 28° (benzoate, m.p. 90°); 2 : 4 : 5-trimethoxyphenol, m.p. 59—61°; 2 : 5-dimethoxy-3 : 4-methylenedioxyphenol, m.p. 84°; 2 : 3 : 4-trimethoxyphenyl benzoate, dimorphic, m.p. 70° and 80°. R. S. C.

**Ethylenic stereoisomerism. V. Molecular compounds of stereoisomeric ethylenes [stilbenes].** C. Weygand and T. Siebenmark (*Ber.*, 1940, 73, [B], 765—770; cf. A., 1939, II, 36).—*cis*-(*p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH)<sub>2</sub>, prepared by half-reduction of (*p*-OMe·C<sub>6</sub>H<sub>4</sub>·C)<sub>2</sub>, is contaminated with the *trans*-form and (*p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>)<sub>2</sub>; it exists in a stable, m.p. 37°, and metastable form, m.p. 36°. *m*-Methoxy-*α*-*m*-anisylcinnamic acid (prep. from *m*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CO<sub>2</sub>Na, *m*-OMe·C<sub>6</sub>H<sub>4</sub>·CHO, and Ac<sub>2</sub>O at 90° and then 160—170°), m.p. 167°, with Cu chromite in quinoline at 230° gives *cis*-3 : 3'-dimethoxystilbene (I), b.p. 133°/0.2 mm., converted by illumination (ultra-violet) in C<sub>6</sub>H<sub>6</sub> into the *trans*-isomeride, m.p. 165°. 2 : 2'-Dimethoxybenzildihydrazone, m.p. ~230° (decomp.), and HgO in boiling xylene (not C<sub>6</sub>H<sub>6</sub>) give 2 : 2'-*o*-anisylotetrazine, N<CR-CR>N (R = *o*-anisyl), m.p. 138°, and a small amount of 2 : 2'-dimethoxytolane, m.p. 126°. *o*-Methoxy-*α*-*o*-anisylcinnamic acid (prep. as above), m.p. 210°, gives, as above, *cis*-2 : 2'-dimethoxy-

*tilbene* (II), m.p. 86—88°, and thence (irradiation) the *trans*-form (together with a substance, m.p. 193°). Methoxystilbenes and *s*-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub> (III) in AcOH give additive compounds as follows: 2(III) + 1 mol. of *cis*-2:2', m.p. 102—103° (IV), *cis*-4:4', m.p. 62—90°, *trans*-3:3', m.p. 137—138°, and *trans*-4:4'-(OMe)<sub>2</sub>, m.p. 155°; 1(III) + 1 mol. of *trans*-2:2'-(OMe)<sub>2</sub>, m.p. 102—103°. With C<sub>10</sub>H<sub>8</sub> in EtOH, (IV) ppts. the additive compound, C<sub>10</sub>H<sub>8</sub> + (III), and the filtrate yields (II). *trans*-(CHBz)<sub>2</sub> and its 4:4'-Me<sub>2</sub>, 4:4'-Et<sub>2</sub>, and 4-Me derivatives give additive compounds, containing 2 mols. of 2:4:6:1-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>·OH; no such compounds are obtained from the *cis*-isomerides, nor from the *cis*- or *trans*-4:4'-Pr<sup>a</sup><sub>2</sub> or 4-Et derivative. The theoretical expectation that the *cis*-forms, richer in energy, would combine with more (III) etc. is not justified. Steric causes may play a predominant rôle. R. S. C.

**Phenolic constituents of pine heart-wood. Synthesis of pinosylvin dimethyl ether [3:5-dimethoxystilbene].** G. Aulin-Erdtman and H. Erdtman (*Ber.*, 1941, 74, [B], 50—56; cf. A., 1939, II, 259).—2:6-Dibromopinosylvin Me<sub>2</sub> ether (I) [from pinosylvin Me<sub>2</sub> ether (II) and Br in CHCl<sub>3</sub>], m.p. 135—136°, on oxidation (KMnO<sub>4</sub>) affords BzOH (85%) and 3:5:2:6:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Br·CO<sub>2</sub>H (III). (I) or (II) is further brominated to *tetrabromopinosylvin Me<sub>2</sub> ether*, forms, m.p. 195—197° (IV) and 172—173°, which give no colour with C(NO<sub>2</sub>)<sub>4</sub> or conc. H<sub>2</sub>SO<sub>4</sub>. 3:4:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CH:CHPh·CO<sub>2</sub>H is decarboxylated (Cu chromite in boiling quinoline) to 3:4:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CH:CHPh (45%), m.p. 111°; 3:5-dimethoxy-*α*-phenylcinnamic acid (70%), m.p. 202—204° [from 3:5:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO and CH<sub>2</sub>Ph·CO<sub>2</sub>H, and PbO in boiling Ac<sub>2</sub>O], similarly gives (mainly) isopinosylvin Me<sub>2</sub> ether (V), b.p. 150° (bath)/0.2 mm., oxidised to BzOH (54%) and 3:5:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>H (32%). The 2:6-Br<sub>2</sub>-derivative (VI), m.p. 173—174°, of (V) is oxidised to BzOH (67%) and (III) (48%). (V) or (VI) is brominated to (IV). When (V) is heated to the b.p. (>350°), (II) is formed in practically 100% yield. J. W. A.

**Preparation of diazonaphthols and nitration of 4-bromoacet-1-naphthalide.** H. H. Hodgson and S. Birtwell (*J.C.S.*, 1943, 321—322).—4-Nitro-, m.p. 130—133° (decomp.), 4-bromo-, m.p. 133° (decomp.), 4-chloro-, m.p. 138° (decomp.), and 4-iodo-naphthalene-1:2-diazo-oxide, m.p. 142° (decomp.), are prepared from 2:4:1-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·R·NH<sub>2</sub> by one or more of four methods given for "diazotisation." Nitration [HNO<sub>3</sub> (d 1.42)—AcOH at 50—65°] of 4:1-C<sub>10</sub>H<sub>6</sub>·Br·NHAc is inhibited by CO(NH<sub>2</sub>)<sub>2</sub>; 2:4:1-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·Br·NHAc has new m.p. 231—233°. 2:4:1-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·Cl·NH<sub>2</sub> and -NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·Br·NH<sub>2</sub> (improved preps.) exhibit chromoisomerism. J. H. B. A.

**Nuclear alkylation of amino-substituted aromatic ethers.**—See B., 1943, II, 275.

**4:4'-Diaminodiphenyl sulphone-2-sulphonamide.**—See B., 1943, III, 225.

**Synthesis and rearrangement of deca- and tetra-hydronaphthalene diols.** J. English, jun., and G. Cavaglieri (*J. Amer. Chem. Soc.*, 1943, 65, 1085—1089).—1-Keto-*cis*-decahydronaphthalene [does not rearrange under the conditions of Hückel (A., 1925, i, 258)] and MgMeI in Et<sub>2</sub>O give 1-methyl-*cis*-decahydro-1-naphthol (90%), b.p. 76—77°/12 mm. 1-Methyl-*trans*-decahydro-1-naphthol, b.p. 93°/5 mm., is dehydrated by KHSO<sub>4</sub> at 120—130° to mixed 1-methyl-Δ<sup>1:2</sup>-*trans*- and -Δ<sup>1:9</sup>-octahydronaphthalene, b.p. 65°/5 mm., which with BzO<sub>2</sub>H in CHCl<sub>3</sub> at 0° give mixed epoxides, b.p. 83°/7 mm. The mixture is hydrated by 10% H<sub>2</sub>SO<sub>4</sub> at 0—10° to 1:2-*trans*-dihydroxy-1-methyl-*trans*- (I) (36%), +3H<sub>2</sub>O, m.p. 79, and 1:9-*trans*-dihydroxy-1-methyl-decahydronaphthalene (II) (15%), m.p. 97°, converted by Pb(OAc)<sub>4</sub>—AcOH at 40—45° into β-2-acetylcyclohexyl-propionic acid, cryst. (ψ-benzylthiocarbamide salt, m.p. 156.5—157.5°; with some propaldehyde), and 2-δ-keto-*n*-amylcyclohexanone, an oil [disemicarbazone, m.p. 207—209° (decomp.)], respectively. In boiling 30% H<sub>2</sub>SO<sub>4</sub>, (I) gives 2-keto-1-methyl-*trans*-decahydronaphthalene (III), b.p. 98°/10 mm. [semicarbazone, m.p. 208—209° (decomp.); oxime, m.p. 149°; 2:4-dinitrophenylhydrazones, m.p. 170—171° (decomp.)], and a small amount of (?) 1-methyl-3:4:5:6:7:10-hexahydronaphthalene (IV), b.p. 82°/7 mm. The structure of (III) is proved by Clemmensen reduction to 1-methyl-*trans*-decahydronaphthalene, b.p. 54°/4 mm., which with Pd—C—H<sub>2</sub> at 350° gives 1-C<sub>10</sub>H<sub>7</sub>Me. In boiling 30% H<sub>2</sub>SO<sub>4</sub>, (II) gives (IV) and a small amount of (?) 1-keto-9-methyldecahydronaphthalene [semicarbazone, m.p. 200—202° (decomp.)]. KHSO<sub>4</sub> at 120—130° dehydrates 1-methyl-1:2:3:4-tetrahydro-1-naphthol to 1-methyl-3:4-dihydronaphthalene, b.p. 84°/5 mm., which with BzO<sub>2</sub>H in CHCl<sub>3</sub> at 0°, gives, by oxidation and rearrangement, 2-keto-1-methyl-3:4-dihydronaphthalene, b.p. 103°/3 mm. {semicarbazone, m.p. 194° (decomp.) [lit. 200—202° (decomp.)]} (and polymerides), and with KMnO<sub>4</sub> in COMe<sub>2</sub> at -40° (later room temp.) gives 1:2-*cis*-dihydroxy-1-methyl-1:2:3:4-tetrahydronaphthalene (~60%, variable), b.p. 135—140°/4 mm., rearranged in boiling 30% H<sub>2</sub>SO<sub>4</sub> to 2-keto-1-methyl-1:2:3:4-tetrahydronaphthalene, b.p. 105—107°/3 mm. [semicarbazone, m.p. 194° (decomp.)]. 1-Keto-2-methyl-1:2:3:4-tetrahydronaphthalene (semicarbazone, m.p. 199°) has b.p. 98°/3 mm. Contrary to Musser *et al.* (A., 1938, II,

182), hydrogenation of α-C<sub>10</sub>H<sub>7</sub>·OH gives mainly the *trans*-decahydro-1-naphthol. R. S. C.

**Synthesis of camphononic acid and *dl*-pinonic acid.**—See A., 1943, II, 306.

**Course of reaction in the transformation of α-dibromoacetophenone into mandelic acid by aqueous alkali.** E. B. Ayres and C. R. Hauser (*J. Amer. Chem. Soc.*, 1943, 65, 1095—1096).—Passing 5% NaOH through CPh·CHBr<sub>2</sub> at 15° and then immediately into 10% AcOH gives 15% of BzCHO, which is thus an intermediate in the formation of OH·CHPh·CO<sub>2</sub>H. The reaction mechanism is discussed. R. S. C.

**Methoxyphenylacetic acids.** H. A. Weidlich and M. Meyer-Delius (*Ber.*, 1940, 73, [B], 631; cf. A., 1943, II, 229).—The methods used in the prep. of methoxyphenylacetic acids (*loc. cit.*) have been described by Hahn *et al.* (A., 1939, II, 368). A. T. P.

**Wandering of halogen atoms in carbon chains and rings.**—See A., 1943, II, 216.

**Catalytic dehydrogenation of 2-substituted 5:6:7:8-tetrahydronaphthalene derivatives.** M. S. Newman and H. V. Zahm (*J. Amer. Chem. Soc.*, 1943, 65, 1097—1101).—Dehydrogenations below are effected by 20% Pd—C (prep. described) at 210—310° (N<sub>2</sub>). CO<sub>2</sub>Me in a side-chain is unaffected by dehydrogenation; thus R·[CH<sub>2</sub>]<sub>n</sub>·CO<sub>2</sub>Me (R = 5:6:7:8-tetrahydro-2-naphthyl here and below) (*n* = 0—3) gives 2-C<sub>10</sub>H<sub>7</sub>·[CH<sub>2</sub>]<sub>n</sub>·CO<sub>2</sub>Me. Ketonic CO adjacent to R is reduced to CH<sub>2</sub>; thus COMeR (prep. by a Friedel-Crafts reaction in CS<sub>2</sub> at <10°), b.p. 132.5—134.5°/3.5—4 mm., gives 63% of 2-C<sub>10</sub>H<sub>7</sub>Et and some 2-C<sub>10</sub>H<sub>7</sub>·COMe [semicarbazone, m.p. 222—223° (decomp.)], and Me γ-keto-γ-5:6:7:8-tetrahydro-2-naphthylbutyrate [prep. by (CH<sub>2</sub>CO)<sub>2</sub>O—AlCl<sub>3</sub>—C<sub>6</sub>H<sub>6</sub> and subsequent esterification of the acid (I), m.p. 114—116°, f.p. 31.0°, b.p. 170—172°/1.5—2 mm., gives 70% of 2-C<sub>10</sub>H<sub>7</sub>·[CH<sub>2</sub>]<sub>3</sub>·CO<sub>2</sub>Me + the derived acid [obtained by reduction of the OH-ester, which then (a) is dehydrated and reduced and (b) lactonises by loss of MeOH and is then hydrogenolysed (see below)]. C·O·X adjacent to R is hydrogenolysed; thus γ-5:6:7:8-tetrahydro-2-naphthyl-γ-butyrolactone [obtained from (I) by Na—Hg], f.p. 33.2°, b.p. 173—175°/1 mm., gives 71% of 2-C<sub>10</sub>H<sub>7</sub>·[CH<sub>2</sub>]<sub>3</sub>·CO<sub>2</sub>H, and CH<sub>2</sub>R·OH gives 67% of 2-C<sub>10</sub>H<sub>7</sub>Me + RMe. 5:6:7:8-Tetrahydro-2-naphthaldehyde (II) (prep. by Rosenmund reduction of the acid chloride in cymene), b.p. 116—119°/3 mm. [semicarbazone, m.p. 223—224° (decomp.)], gives C<sub>10</sub>H<sub>8</sub> and tetrahydronaphthalene. Me β-5:6:7:8-tetrahydro-2-naphthylacrylate [(II) and CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> in C<sub>6</sub>H<sub>5</sub>N at 100° afford the acid (III), m.p. 170.8—171.8°, m.p. 40°, b.p. 157—158°/2.5—3 mm., gives 2-C<sub>10</sub>H<sub>7</sub>·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>Me (89%). α-5:6:7:8-Tetrahydro-2-naphthylethyl alcohol [prep. from COMeR by Al(OPr<sup>β</sup>)<sub>3</sub> in Pr<sup>β</sup>OH; if the reaction mixture is allowed to become hot during isolation 2-vinyl-5:6:7:8-tetrahydronaphthalene, b.p. 96°/2 mm., results], b.p. 120—121°/2 mm., gives a polymeride and a little 2-C<sub>10</sub>H<sub>7</sub>Et. RCOCl gives a mixture. The following are incidentally described. RCO<sub>2</sub>H [prep. from COMeR by Ca(OCl)<sub>2</sub>—Na<sub>2</sub>CO<sub>3</sub>—NaOH—H<sub>2</sub>O—dioxan at 100°], m.p. 154—155° (chloride, b.p. 121—122°/2 mm.; Me ester, b.p. 149—150°/4—4.5 mm.). CH<sub>2</sub>R·OH [from RCHO by H<sub>2</sub>—PtO<sub>2</sub>—FeCl<sub>2</sub> (trace) in EtOH], b.p. 133—134°/4 mm. Me 5:6:7:8-tetrahydro-2-naphthylacetate (from CH<sub>2</sub>R·OH by, successively, SOCl<sub>2</sub>, NaCN—MeOH—H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>—H<sub>2</sub>O—AcOH, and HCl—MeOH), b.p. 141—143°/4 mm. (acid, m.p. 97—97.5°). Me β-5:6:7:8-tetrahydro-2-naphthylpropionate, b.p. 136—137.5°/2.5—3 mm. [acid, m.p. 81—82° (cf. lit.)], obtained with some bimol. product from (III) by Na—Hg—Ni (trace) in neutral solution and subsequent esterification. γ-5:6:7:8-Tetrahydro-2-naphthylbutyric acid [from (I) by Clemmensen reduction], m.p. 47—49°, b.p. 195—200°/4.5—5 mm. (Me ester, b.p. 181—184°/3.5—4 mm.). M.p. are corr. R. S. C.

**Preparation of aminobenzoic acid esters of substituted monoalkyl-amino-alcohols.** W. F. Ringk and E. Epstein (*J. Amer. Chem. Soc.*, 1943, 65, 1222—1226).—NHR·CH<sub>2</sub>·CMe<sub>2</sub>·OH (R = *n*-hexyl, b.p. 224—228°, *n*-heptyl, b.p. 242—246°, β-octyl, b.p. 245—248°, and β-ethyl-*n*-hexyl, b.p. 245—248°) (prep. as A., 1940, II, 85, but in 50% Pr<sup>β</sup>OH; yields ~45%) with *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·COCl (I) in aq. alkali give solid esters, reduced by Fe—HCl etc. to β-*n*-hexyl-, m.p. 169—171°, β-*n*-heptyl-, m.p. 169—172°, β-β'-octyl-, +0.5H<sub>2</sub>O, m.p. 154—156°, and β-β'-ethyl-*n*-hexyl-, m.p. 141—143°, -amino-tert-butyl *p*-aminobenzoate sulphate, B<sub>2</sub>H<sub>2</sub>SO<sub>4</sub> (corresponding hydrochlorides are oils). NH<sub>2</sub>·CMe<sub>2</sub>·CH<sub>2</sub>·OH with AlkHal in boiling Pr<sup>β</sup>OH gives 20—60% of β-ethyl-, m.p. 72—73°, b.p. 167—169°, β-*n*-, m.p. 55—57°, b.p. 183—186°, and -iso-propyl-, m.p. 40—42°, b.p. 172—175°, β-*n*-, m.p. 68—69°, b.p. 200—203°, -iso-, m.p. 45—46°, b.p. 192—194°, and -sec-butyl-, b.p. 186—190°; β-*n*-, m.p. 59—60°, and -iso-amyl-, m.p. 73—74°, b.p. 211—215°, β-*n*-hexyl-, m.p. 62—63°, b.p. 235—238°, β-*x*-ethylbutyl-, b.p. 220—226°, β-*n*-heptyl-, m.p. 50—52°, b.p. 253—258°, β-β'-octyl-, b.p. 250—255°, β-β'-ethyl-*n*-hexyl-, m.p. 15—17°, b.p. 249—255°, and β-*n*-decyl-, m.p. 55—57°, b.p. 295—300°, -isobutyl alcohol, converted by (I) in aq. NaOH at 35—40° and then Fe—HCl into β-ethyl-, m.p. 245—246.5°, β-*n*-, m.p. 239—240°, and -iso-propyl-, m.p. 234.5—236°, β-*n*-, m.p. 192—192.5°.

-iso-, m.p. 225.8—228°, and -sec.-butyl-, +H<sub>2</sub>O, m.p. 202—205°,  $\beta$ -n-, m.p. 209—211.8°, and -iso-amyl-, m.p. 202—203°,  $\beta$ -n-hexyl-, m.p. 212.5—213.5°,  $\beta$ -x-ethylbutyl-, m.p. 198—199.5°,  $\beta$ -n-heptyl-, m.p. 197—198°,  $\beta$ - $\beta'$ -octyl- (II), +0.5H<sub>2</sub>O, m.p. 137—140°,  $\beta$ - $\beta'$ -ethyl-n-hexyl-, m.p. 154—158°, and  $\beta$ -n-decyl-, m.p. 141—142°, -iso-butyl p-aminobenzoate hydrochloride.  $\beta$ -Ethyl- (sulphate, m.p. 223—224°),  $\beta$ -n- (hydrochloride, m.p. 192—194°) and -iso-propyl- (sulphate, m.p. 188—189°),  $\beta$ -n- (hydrochloride, m.p. 205—208°) and -iso-butyl- (sulphate and hydrochloride, oils) -aminoisobutyl m- and  $\beta$ -n-butyl-aminoisobutyl o-aminobenzoate, m.p. 68—69° (hydrochloride, sulphate, and phosphate, oils), are similarly prepared.  $p$ -NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·NHBu<sup>a</sup>, when kept for several weeks, isomerises to  $p$ -nitrobenz-N- $\beta$ -hydroxyethyl-N-butylamide, m.p. 195—196° (cf. Kremer *et al.*, A., 1942, II, 283). Pharmacological data are reported for the esters. The iso- are very potent anaesthetics and less toxic than the *tert*.-butyl esters. They are vasodilators in cats (intravenous injection), but are synergistic with adrenaline. The most effective product is (II), which is 24 times as effective as cocaine for surface anaesthesia and 8 times as effective as procaine for conductive anaesthesia.

R. S. C.

**$\beta$ -Diaryladipic acids.**—See B., 1943, II, 276.

**Conversion of an alcohol into the corresponding aldehyde by a less volatile aldehyde with the aluminium alkoxide as catalyst.** Influence of an ethylene linking in the reactant aldehyde. R. R. Davies and H. H. Hodgson (*J.S.C.I.*, 1943, 62, 109—110).—Al alkoxides act as catalysts for the conversion of the alcohol into the corresponding aldehyde through reaction with a less volatile aldehyde. Cinnamaldehyde is a more reactive aldehyde than PhCHO due to its ethylenic linking. An explanation of the reaction is given based on H bonding.

**Alkylation and other reactions of 9-formylfluorene.** W. G. Brown and B. A. Bluestein (*J. Amer. Chem. Soc.*, 1943, 65, 1082—1084).—9-Formylfluorene (I) [prep. from fluorene by HCO<sub>2</sub>Et and KOEt (80—90%) or NaOEt (65%) in Et<sub>2</sub>O], b.p. 189—192°/10 mm., unstable, with Me<sub>2</sub>SO<sub>4</sub>-KOH-H<sub>2</sub>O gives 62% of the *enol Me ether*, m.p. 104°, but with MeI-KOH-H<sub>2</sub>O gives 9-methyl- (II), and with Pr <sup>$\beta$</sup> Br, cyclohexyl bromide, or CH<sub>2</sub>PhCl in KOH-aq. EtOH gives 9-isopropyl-, m.p. 54—55°, 9-cyclohexyl-, m.p. 115—116° [not identical with the compound, m.p. 102—103°, of Miller *et al.* (A., 1935, 741)], or 9-benzyl-fluorene (77%), m.p. 132—133° (also obtained from Et 9-fluorenylglyoxylate and CH<sub>2</sub>PhCl in boiling NaOH-H<sub>2</sub>O-EtOH), respectively. With CH<sub>2</sub>O in aq. NaOH, (I) gives 9-fluorenylcarbinol (III). Hydrogenation (PtO<sub>2</sub>; EtOH; 3 atm.) of the *enol acetate* or benzoate of (I) gives (II) and the acetate or benzoate, respectively, of (III). The K salt of (I) with ClCO<sub>2</sub>·CH<sub>2</sub>Ph in H<sub>2</sub>O gives CH<sub>2</sub>Ph  $\beta\beta$ -2:2'-diphenylenevinyl carbonate, m.p. 149.5°, hydrogenated very slowly to (II) (poor yield).

R. S. C.

**Lignin and related compounds. LXIV. Synthesis and properties of  $\gamma$ -hydroxy- $\gamma$ -4-hydroxy-3-methoxyphenylpropan- $\alpha$ -one.** K. A. West and H. Hibbert. **LXVIII. Synthesis and properties of  $\alpha$ - and  $\gamma$ -ethoxy- $\alpha$ -4-hydroxy-3-methoxyphenylpropan- $\beta$ -one and their methyl ethers.** M. Kulka and H. Hibbert (*J. Amer. Chem. Soc.*, 1943, 65, 1170—1172, 1185—1187; cf. A., 1942, II, 158).—LXIV. Veratrole, Cl·[CH<sub>2</sub>]<sub>2</sub>·COCl, and AlCl<sub>3</sub> (4 mols.) in CS<sub>2</sub> at 50° and then at 100° (no solvent) give 4-hydroxy-3-methoxy- $\beta$ -chloropropiophenone (I) (60%), m.p. 101—102°, converted by KOAc-AcOH at 100° into 4-hydroxy-3-methoxy- $\beta$ -acetoxyp- (II) (67%), m.p. 80—81°, and thence (BaCO<sub>3</sub> in boiling H<sub>2</sub>O) - $\beta$ -hydroxy-propiophenone (III) (55%), m.p. 109—110°. CH<sub>2</sub>N<sub>2</sub>-Et<sub>2</sub>O converts (I), (II), and (III) into the known veratrole derivatives. With Et<sub>2</sub>SO<sub>4</sub>-1.5% NaOH at the b.p., (II) gives the Et ether, oxidised by KMnO<sub>4</sub> to 3:4:1-OMe·C<sub>6</sub>H<sub>3</sub>(OEt)·CO<sub>2</sub>H. With 2% HCl-EtOH, (III) gives 4-hydroxy-3-methoxy- $\beta$ -ethoxypropiophenone, forms, m.p. 72—74° and 35—37° (with CH<sub>2</sub>N<sub>2</sub> gives the veratrole derivative). 72% H<sub>2</sub>SO<sub>4</sub> at room temp. or boiling 5% H<sub>2</sub>SO<sub>4</sub> or 1% NaOH converts (III) into lignin-like products.

LXVIII.  $\alpha$ -Ethoxy- $\alpha$ -4-acetoxyp- (prep. from the 4-Br-compound by AgOAc in boiling EtOH), an oil, with NaOEt-EtOH at room temp. gives  $\alpha$ -ethoxy- $\alpha$ -4-hydroxy-3-methoxyphenylpropan- $\beta$ -one (80%), m.p. 62—63° (semicarbazone, m.p. 173.5—174.5°), methylated by CH<sub>2</sub>N<sub>2</sub> to  $\alpha$ -ethoxy- $\alpha$ -3:4-dimethoxyphenylpropan- $\beta$ -one (2:4-dinitrophenylhydrazones, m.p. 141—142°).  $\beta$ -Nitro- $\gamma$ -ethoxy- $\alpha$ -4-hydroxy-3-methoxyphenyl- $\Delta^a$ -propene (from vanillin by NO<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·OEt, a little NH<sub>2</sub>Me·HCl, and Na<sub>2</sub>CO<sub>3</sub> in EtOH at room temp.; 30% yield), m.p. 78—79°, with Fe-FeCl<sub>3</sub>-HCl-EtOH-H<sub>2</sub>O at the b.p. and then 7N-H<sub>2</sub>SO<sub>4</sub> at room temp. gives  $\gamma$ -ethoxy- $\alpha$ -4-hydroxy-3-methoxyphenylpropan- $\beta$ -one (68%), an oil (semicarbazone, m.p. 144—144.5°). 3:4:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO gives similarly  $\beta$ -nitro- $\gamma$ -ethoxy- $\alpha$ -3:4-dimethoxyphenyl- $\Delta^a$ -propene, m.p. 90—91°, and  $\gamma$ -ethoxy- $\alpha$ -3:4-dimethoxyphenylpropan- $\beta$ -one (67%) (2:4-dinitrophenylhydrazones, m.p. 114—116°).

R. S. C.

**Synthesis of  $\alpha$ -acyltetronic acids.**—See A., 1943, II, 217.

**Friedel-Crafts reaction of lactones. III. Dehydrogenations with aluminium chloride.** H. Beyer and H. Schulte (*Ber.*, 1941, 74, [B], 98—106; cf. A., 1937, II, 291, 377).—CH<sub>2</sub>Bz·CO<sub>2</sub>Et, NaOEt, and

epichlorohydrin in EtOH afford  $\delta$ -chloro- $\alpha$ -benzoyl- $\gamma$ -valerolactone (I), m.p. 105—106° ( $p$ -nitrophenylhydrazones, m.p. 159°), which with C<sub>6</sub>H<sub>6</sub> and AlCl<sub>3</sub> at 80—90° for 1 week gives acidic products (A), 1-benzoyl-1:2:3:4-tetrahydronaphthalene (II), b.p. 182—183°/0.5 mm. (semicarbazone, sinters at 168°, m.p. 171°), and Ph  $\gamma\delta$ -diphenyl-n-butyl ketone (III), m.p. 108—109° (semicarbazone, m.p. 180—181°;  $p$ -nitrophenylhydrazones, m.p. 137—138°). (II) is reduced (H<sub>2</sub>, PtO<sub>2</sub>) to phenyl-1:2:3:4-tetrahydro-1-naphthylcarbinol, b.p. 186—187°/0.6 mm., m.p. 101°, and (Clemmensen) to 1-benzyl-1:2:3:4-tetrahydronaphthalene, b.p. 145—146°/0.6 mm., which is also obtained by Clemmensen reduction of 1-keto-4-benzyl-1:2:3:4-tetrahydronaphthalene. Clemmensen reduction of (III) gives  $\alpha\beta\epsilon$ -triphenyl-pentane, b.p. 206—207°/0.18 mm., m.p. 39—40°. (A) contains 1:2-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (hydrazide, m.p. 212—213°) which must be formed from (I) by loss of PhMe.

J. WA.

**Properties of 4-methoxydibenzoylmethane [benzoylanisoylmethane].** R. P. Barnes and A. Brandon (*J. Amer. Chem. Soc.*, 1943, 65, 1070—1072).— $p$ -OMe·C<sub>6</sub>H<sub>4</sub>·CO·CH·CHPh and Br in CS<sub>2</sub>-CCl<sub>4</sub> give the dibromide (I), m.p. 162°, converted by KOAc in boiling AcOH into  $p$ - $\alpha$ -bromo-, an oil, which with boiling NaOMe-MeOH gives  $p$ - $\beta$ -methoxy-, semi-cryst., -cinnamoylanisole. With conc. HCl-MeOH this gives  $p$ - $\beta$ -hydroxycinnamoylanisole (II), m.p. 128—129°, which with NH<sub>2</sub>OH·HCl in boiling aq. MeOH yields 5-phenyl-3- $p$ -anisylisooxazole (III), m.p. 119°, also obtained from (I) by NH<sub>2</sub>OH·HCl-EtOH-H<sub>2</sub>O and then KOH. Identity of (III) with the misnamed isooxazole of Pond *et al.* (A., 1901, i, 35) is due to the compound considered to be  $p$ -OMe·C<sub>6</sub>H<sub>4</sub>·C(OH)·CH·COPh reacting as and being identical with (II).

R. S. C.

**Optical activity in the *trans*-hydrindane and -decahydronaphthalene series.** W. Hüchel and H. Sowa (*Ber.*, 1941, 74, [B], 57—63).—The remarkable high rotation of optically active *trans*- $\beta$ -hydrindanone (I) suggested investigating whether a symmetrical ring system with *trans*-fusion of the rings gave rise to so high a rotation or whether it was to be attributed to the induced dissymmetry of the CO group. Distillation of (+)-cyclohexane-1:2-diacetic acid (II),  $[\alpha]_D^{20} +48.35^\circ$  in EtOH, affords (-)-(I),  $[\alpha]_D^{20} -301.8^\circ$  in C<sub>6</sub>H<sub>6</sub>, which is reduced (H<sub>2</sub>, Pt-black, AcOH) to a mixture of (-)-*trans*-hydrindane, b.p. 159°/760 mm.,  $[\alpha]_D^{20} -5.98^\circ$ , and (-)-*trans*- $\beta$ -hydrindanol, m.p. 12°,  $[\alpha]_D^{20} -12.46^\circ$  (homogeneous), -7.83° in C<sub>6</sub>H<sub>6</sub>, -9.77° in tetrahydronaphthalene, -11.95° in cyclohexane, -14.07° in EtOH (phenylurethane, m.p. 131—132°,  $[\alpha]_D^{20} -18.67^\circ$  in EtOH), isolated as the H succinate, m.p. 48—50°. Impure *trans*-decahydro- $\beta$ -naphthylamine II (III) and HCO<sub>2</sub>H at 120° afford the formate, m.p. 124°, and formyl derivative, m.p. 84°, hydrolysed to pure (III), m.p. 15° (Ac derivative, m.p. 163°). (III) is resolved through the  $\alpha$ -bromo-d-camphorsulphonate, m.p. 158°,  $[\alpha]_D^{20} +71.7^\circ$  in EtOH, to (+)-(III), m.p. 10.6°,  $[\alpha]_D^{20} +2.14^\circ$  (hydrochloride,  $[\alpha]_D^{20} +0.92^\circ$  in H<sub>2</sub>O; Ac, m.p. 175—176°,  $[\alpha]_D^{20} +25.3^\circ$  in EtOH, and Bz derivative, m.p. 174°,  $[\alpha]_D^{20} +1.89^\circ$  in EtOH). Impure (-)-(III) is isolated from the mother-liquors as the H tartrate and consists of 75% of (-)- and 25% of (+)-base. (+)-(III) with NaNO<sub>2</sub> in 10% AcOH gives (?) decahydro- $\beta$ -naphthol II (IV), m.p. 72°,  $[\alpha]_D^{20} \pm 0^\circ$  in EtOH, -2.7° in (?) cyclohexane, -1.8° in tetrahydrofuran (toluenesulphonate, m.p. 63°,  $[\alpha]_D^{20} -1.75^\circ$  in EtOH), after purification through the H phthalate, m.p. 173°,  $[\alpha]_D^{20} -1.4^\circ$  in EtOH. The toluenesulphonate of (IV) and NaOEt give a mixture of (IV), decahydronaphthyl Et ether (formed with Walden inversion), b.p. 100°/15 mm., and (-)-*trans*- $\Delta^2$ -octahydronaphthalene, b.p. 72°/13 mm.,  $[\alpha]_D^{20} -26.2^\circ$ , which is oxidised (KMnO<sub>4</sub>) to optically impure (II), m.p. 151°,  $[\alpha]_D^{20} +40.5^\circ$ , containing ~10% of (-)-(II), indicating ~90% resolution of (III).

J. WA.

**Oxido-ketones in the indene series.** C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1943, 65, 1230—1235).—4:5-Dibromo- $\alpha$ -benzylidene-, m.p. 244°, and  $\alpha$ -benzylidene-4:5-dimethylphthalide, m.p. 166°, and thence 5:6-dibromo-2:3-diphenyl-, m.p. 196°, and 2:3-diphenyl-5:6-dimethyl-1-indenone, m.p. 229°, are prepared (method: A., 1943, II, 196). Adding 15% H<sub>2</sub>O<sub>2</sub> to the appropriate indenone and aq. NaOH in EtOH at, usually, 60—70° gives 2:3-epoxy-2:3-diphenyl-5:6-dimethyl-, m.p. 197°, 5:6-dibromo-2:3-epoxy-2:3-diphenyl-, m.p. 178°, and 2:3-epoxy-2:3:5:6-tetraphenyl- (I), m.p. 199—200°, -1-indanone, but 2:3:5:6-tetraphenyl-4:7-dimethyl- and 2:3:4:7-tetraphenyl-indenone do not thus react. The epoxy-compounds are peroxidic, liberating I from KI-AcOH; with dry HCl-AcOH at room temp., hydrolysis to 2:3-dihydroxy-2:3-diphenyl-5:6-dimethyl- (II), m.p. 145°, -2:3:5:6-tetraphenyl- (III), m.p. 215°, and 4:5-dibromo-2:3-dihydroxy-2:3-diphenyl-1-indanone, m.p. 166°, occurs, but in hot HCl-AcOH or usually, very slowly, AcOH alone 3:4-diphenyl-6:7-dimethyl- (IV), m.p. 208°, 3:4:6:7-tetraphenyl- (V), m.p. 230°, and 6:7-dibromo-3:4-diphenyl-isocoumarin, m.p. 229°, are obtained. (IV) and (V) are similarly obtained from (II) and (III), respectively; (II) and (III) are thus intermediates, others being the 1:2-epoxy-1:3-dihydroxyindanes (A) and 4-hydroxy-3:4-dihydroisocoumarins. (V) dissolves in aq. NaOH (not Na<sub>2</sub>CO<sub>3</sub>) and then, by careful acidification, yields Ph 2-carboxy- $\alpha$ :4:5-triphenylbenzyl ketone (VI), m.p. 244°, whence it is regenerated by warming alone or in solution. Structures are proved by oxidation of (V) or

(VI) by  $\text{CrO}_3$  or  $\text{KMnO}_4$  to  $\text{BzOH}$  and 4 : 5 : 2 : 1- $\text{C}_6\text{H}_2\text{Ph}_2\text{Bz}\cdot\text{CO}_2\text{H}$ . 2 mols. of  $\text{MgMeI}$  add (Grignard machine) to (V), but the product is dehydrated to give *Ph a* : 4 : 5-triphenyl-2-isopropenylbenzyl ketone, m.p. 256°;  $\text{MgPhBr}$  and (V) give *Ph a* : 4 : 5-triphenyl-2- $\alpha$ -hydroxybenzhydrylbenzyl ketone, m.p. 186°. The other isocoumarins are stated (no details) to behave similarly. Weitz *et al.* (A., 1921, i, 869) misinterpreted the similar reactions of 2 : 3-diphenyl-1-indenone. This yields an epoxide, glycol (VII) (adds 1  $\text{MgMeI}$ ; 2 active H), lactone [which, like (VII), is oxidised to  $\text{BzOH}$  and  $o\text{-C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$ ], and derived acid. Warm alkali destroys (III), but converts (II) or (VII) into respectively 1-benzoyl-2-phenyl-4 : 5-dimethyl-, m.p. 132°, or 1-benzoyl-2-phenyl-isobenzofuran (VIII) (the "yellow substance" of Weitz *et al.*). (VIII) is unimol., adds 1  $\text{MgMeI}$ , contains no active H, does not form a quinoxaline, resists  $\text{H}_2\text{O}_2$ , but is oxidised by  $\text{CrO}_3$  to  $\text{BzOH}$  and  $o\text{-C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$  and by  $\text{KMnO}_4$  or  $\text{HNO}_3$  to  $o\text{-COPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{COPh}$ . Its structure is thus established. Its formation from (VII) occurs by way of  $o\text{-OH}\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{COPh}$  and  $o\text{-C}_6\text{H}_4\text{CHPh}\text{---}\text{CBz(OH)}\text{---}\text{O}$ . Only the epoxide (IX), new m.p. 58—59°, is formed from 3-phenyl-2-ethyl-1-indenone by alkaline  $\text{H}_2\text{O}_2$ . This yields, as above, 2 : 3-dihydroxy-3-phenyl-2-ethyl-1-indanone, m.p. 122°, and 4-phenyl-3-ethylisocoumarin, m.p. 101°. With 30—32%  $\text{HBr}\cdot\text{AcOH}$  at 10—15°, (IX) gives 3-bromo-2-hydroxy-3-phenyl-2-ethyl-1-indanone (80%), m.p. 129°, whence  $\text{MgMeI}$  does not remove the Br. In boiling  $\text{AcOH}$  (6 hr.) or 15%  $\text{HBr}$ —or 30%  $\text{H}_2\text{SO}_4\cdot\text{AcOH}$  (10 min.), (I) gives 4-benzoyl-4-phenyl-2 : 3-4' : 5'-diphenylbenz- $\Delta^2$ -cyclobutenone (X), brick-red, m.p. 219—220°, which adds 2  $\text{MgMeI}$ , contains no active H, is oxidised to  $\text{BzOH}$  and 4 : 5 : 2 : 1- $\text{C}_6\text{H}_2\text{Ph}_2\text{Bz}\cdot\text{CO}_2\text{H}$ , in boiling  $\text{KOH}\cdot\text{EtOH}$  gives (VI), and with  $\text{Zn(OAc)}_2$ ,  $\text{KOAc}$ , or  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in hot  $\text{AcOH}$  gives (V) (reaction mechanism discussed). The CO of epoxy-ketones is very reactive; e.g.,  $\alpha\beta$ -epoxy- $\beta$ -phenylpropiophenone rapidly gives a 2 : 4-dinitrophenylhydrazone, m.p. 205°. The labile grouping,  $\text{CH}\text{---}\text{C(OH)}\cdot$  (B), as in (A) (above), is held to explain various "rearrangements." E.g., oxidation of cyclic ketones to lactones by Caro's acid involves the reactions,  $\text{CH}_2\cdot\text{CO}_2\text{---}\text{CH(OH)}\cdot\text{CO}\cdot\text{---}\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{---}$ ; (B) is also an intermediate in the conversion of  $\text{CHBz}_2\cdot\text{OH}$  into  $\text{CH}_2\text{Bz}\cdot\text{OBz}$  by distillation and of  $\text{CPhBz}_2\cdot\text{OH}$  into  $\text{CHPhBz}\cdot\text{OBz}$ . R. S. C.

**Simple and practical preparation of 2-methyl-1 : 4-naphthaquinone from naphthalene.** P. P. T. Sah, W. Brüll, and H. Holzen (*Ber.*, 1940, 73, [B], 762).—The following reaction series is recommended.  $2\text{-C}_{10}\text{H}_7\cdot\text{SO}_3\text{Na} + \text{K}_4\text{Fe(CN)}_6$  in Cu at <1 atm.  $\rightarrow 2\text{-C}_{10}\text{H}_7\cdot\text{CN} \rightarrow (\text{KOH}\text{---}\text{or NaOH}\cdot\text{EtOH}) 2\text{-C}_{10}\text{H}_7\cdot\text{CO}_2\text{H} \rightarrow [\text{Ba salt} + (\text{HCO}_2)_2\text{Ba}$  in Cu at <1 atm.]  $2\text{-C}_{10}\text{H}_7\cdot\text{CHO}$  (50—60%)  $\rightarrow$  (Clemmensen)  $2\text{-C}_{10}\text{H}_7\cdot\text{Me} \rightarrow 1 : 2 : 4\text{-O:C}_{10}\text{H}_5\text{Me:O}$ , m.p. 105—106° (quinol diacetate, m.p. 112—113°). R. S. C.

**Water-soluble derivatives of menadione [2-methyl-1 : 4-naphthaquinone].** A. R. Menotti (*J. Amer. Chem. Soc.*, 1943, 65, 1209—1211).—1 : 2 : 4- $\text{O:C}_{10}\text{H}_5\text{Me:O}$  (I) with aq.  $\text{NaHSO}_3$  at 0° gives the insol., hygroscopic additive compound (II),  $+3\text{H}_2\text{O}$ , m.p. (capillary)  $\sim 126^\circ$  (immersed at  $115^\circ$ ) or (micro) loses solvent at  $100^\circ$  and melts at  $154\text{—}157^\circ$  (decomp.) (benzylisothiocarbamide salt, m.p.  $126\cdot5\text{—}128^\circ$ ), but at  $90\text{—}100^\circ$  slowly gives 2-methyl-1 : 4-naphthaquinol-3-sulphonic acid (sol. Na salt), isolated as K salt (III),  $+2\text{H}_2\text{O}$ , loses solvent at  $100^\circ$  and melts at  $193\text{—}196^\circ$  (decomp.) [also obtained with much 2 : 1 : 4- $\text{C}_{10}\text{H}_5\text{Me(OH)}_2$  from (II) in boiling  $\text{H}_2\text{O}$ ]. With  $\text{Ac}_2\text{O}\cdot\text{AcOH}$ , (III) gives the K salt diacetate (IV), m.p.  $>205^\circ$  (decomp.). 2 : 1 : 4- $\text{C}_{10}\text{H}_5\text{Me(OAc)}_2$  and  $\text{ClSO}_3\text{H}$  in  $\text{CHCl}_3$  at  $25^\circ$  give, after treatment with  $\text{KCl}$ , K 2-methyl-1 : 4-naphthaquinol-3-sulphonate monoacetate,  $+ \text{H}_2\text{O}$ , m.p. (micro)  $168\text{—}170^\circ$  (decomp.; after loss of solvent at  $\sim 100^\circ$ ), and some (IV). (II) is identified by conversion into (I) (95—98%) by 10% aq.  $\text{NH}_3$ , by Craven's test, or crystallo-optical properties (detailed). (III) is identified by formation of a scarlet ppt. with the  $\text{Fe}^{++}$   $o$ -phenanthroline complex, formation of a red colour in dil. alkali, or crystallo-optical properties (detailed). R. S. C.

**Model experiments on the use of cyclopentadiene in the synthesis of sterol-like compounds.** C. F. Koelsch and F. J. Lucht (*J. Amer. Chem. Soc.*, 1943, 65, 1240—1242).—3-Methylcyclohexenone does not react with cyclopentadiene (I). 1 : 2 : 4- $\text{O:C}_6\text{H}_5\text{Ph:O}$  (improved prep.) and (I) in warm  $\text{MeOH}$  give (?) 2-phenyl-5 : 8-endomethylene-5 : 8 : 9 : 10-tetrahydro-1 : 4-naphthaquinone (88%), m.p.  $70\cdot5\text{—}71^\circ$ , reduced by Zn dust in  $\text{AcOH}$  at  $70^\circ$  to the 2 : 3 : 5 : 8 : 9 : 10- $\text{H}_6$ -quinone (75%), m.p.  $149\cdot5\text{—}152^\circ$ , which by Clemmensen reduction gives a substance,  $\text{C}_{17}\text{H}_{20}$ , b.p.  $136\text{—}138^\circ/4$  mm. Contrary to Niederl *et al.* (A., 1939, II, 416), cyclohexanone and  $m$ -cresol give 4-cyclohexenyl- $m$ -cresol (14%), b.p.  $180\text{—}190^\circ/25$  mm. [and a dimeride, m.p.  $142\text{—}143^\circ$  or  $(+\text{COMe}_2)$  softens  $106^\circ$ , m.p.  $111\text{—}113^\circ$  (decomp.)], hydrogenated ( $\text{PtO}_2$ ;  $\text{AcOH}$ ) to 4-cyclohexyl- $m$ -cresol, m.p.  $69\text{—}70^\circ$ , b.p.  $166\text{—}169^\circ/19$  mm. Coupling with  $p\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  and reduction by  $\text{Na}_2\text{S}_2\text{O}_4$  then yields 6-amino-4-cyclohexyl- $m$ -cresol (78%), pink at  $170^\circ$ , m.p.  $182^\circ$ , oxidised by  $\text{K}_2\text{Cr}_2\text{O}_7\text{---}\text{H}_2\text{SO}_4$  to 2-cyclohexyl-5-methylbenzoquinone, m.p.  $60\text{—}61^\circ$  (derived quinol, m.p.  $146\text{—}148^\circ$ ), which with (I) in boiling  $\text{MeOH}$  gives 2-cyclohexyl-10-methyl-5 : 8-endomethylene-5 : 8 : 9 : 10-tetra-

hydro-1 : 4-naphthaquinone (96%), m.p.  $75\text{—}77^\circ$  (with  $\text{Zn}\cdot\text{AcOH}$  gives a substance, m.p.  $71\text{—}78^\circ$ ). R. S. C.

#### IV.—STEROLS AND STEROID SAPOGENINS.

**Formation of ergostatetraene-B during the acetylation of ergosterol.** H. A. Stansbury, jun. (*J. Amer. Chem. Soc.*, 1943, 65, 1243).—Ergosteryl acetate, prepared from ergosterol by boiling  $\text{Ac}_2\text{O}$ , is accompanied by a small amount of ergostatetraene-B. R. S. C.

**Thiocholesterol.** T. Wagner-Jauregg and T. Lennartz (*Ber.*, 1941, 74, [B], 27—32).—The "thiocholesterol" of Montignie (A., 1931, 481) is a dithiocholesteryl phosphate ( $\text{S} : \text{P} = \sim 2 : 1$ ). Cholesteryl bromide and  $\text{NaCNS}$  in boiling aq.  $\text{EtOH}$  give cholesteryl thiocyanate (I), m.p.  $129^\circ$ ,  $[\alpha]_D -10\cdot97^\circ$ , reduced ( $\text{Zn}\cdot\text{Hg}$ , aq.  $\text{HCl}$ ) to thiocholesterol (II), m.p.  $99\cdot5^\circ$ ,  $[\alpha]_D -23\cdot85^\circ$  [cinnamate, m.p.  $141\text{—}142^\circ$  (turbid),  $224\text{—}226^\circ$  (clear),  $[\alpha]_D -9\cdot96^\circ$ ; chaulmoograte, m.p.  $67\text{—}69^\circ$ ,  $[\alpha]_D -9\cdot28^\circ$ ;  $\text{CH}_2\text{Ph}$  ether, m.p.  $98\cdot5^\circ$ ,  $[\alpha]_D -31\cdot7^\circ$ ]. (I) with  $\text{NaOEt}\cdot\text{EtOH}$ ,  $\text{KOH}\cdot\text{aq. EtOH}$ , or  $\text{K}_2\text{CO}_3\text{---}\text{C}_6\text{H}_{11}\cdot\text{OH}$  affords dicholesteryl disulphide, m.p.  $144\cdot5^\circ$ ,  $[\alpha]_D -41\cdot78^\circ$ , which is reduced ( $\text{Zn}\cdot\text{Hg}$ , aq.  $\text{HCl}$ ,  $\text{PhMe}$ ) to (II).  $[\alpha]$  are in  $\text{CHCl}_3$ . J. WA.

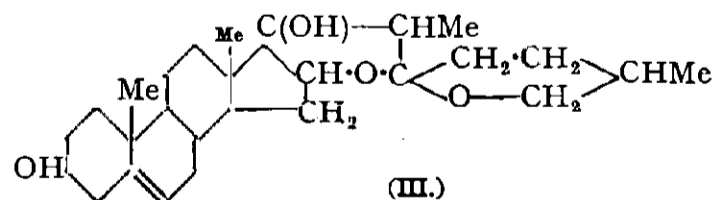
**Deoxycholic acid. Preparation from cholic acid.** G. A. D. Haslewood (*Chem. Products*, 1943, 6, 65—66).—An account of work previously abstracted (A., 1942, II, 365; 1943, II, 199). Lithocholic acid is a by-product and arises from 3-hydroxy-7 : 12-diketocholanic acid. S. A. M.

**Bile acids. LX.** M. Schenck (*Z. physiol. Chem.*, 1940, 264, 267—273).—When 7-nitrodeoxybilanic acid (I) is treated with  $\text{HNO}_3$  ( $d$  1.4) for 48 hr. at room temp., 6-nitrodeoxybilanic acid (II) is formed. (II) is also formed from bilanic acid dioxime and  $\text{HNO}_3$ ; in this case (I) is an intermediate. 6-Aminobilanic acid, which reduces  $\text{AgNO}_3\text{---}\text{NH}_3$  on heating, is oxidised to cilianic acid by Fehling's solution. J. N. A.

**Behaviour of  $\Delta^1$ -unsaturated steroid ketones on reduction by fermenting yeast.** A. Butenandt, H. Dannenberg, and L. A. Surányi (*Ber.*, 1940, 73, [B], 818—820).—Yeast fermenting in aq. sucrose reduces  $\Delta^1$ -androstene-3 : 17-dione or  $\Delta^1$ -androstene-17-ol-3-one to isoandrostane-3 : 17-diol, but does not affect  $\Delta^1$ -cholestenone or  $\Delta^1$ -allopregnenedione. The position of the C:C and the nature of the  $\text{C}_{17}$ -substituent thus both affect the reducibility of the  $\Delta^1$ -ketones. R. S. C.

**Sterols. CLIV—CLVII. Sapogenins. LXVI. Sapogenin of *Trigonella foenum-graecum*. LXVII. Pennogenin, nologenin, and fesogenin, three new sapogenins from *Beth* root. LXVIII. Steroidal sapogenin from *Balanites aegyptica*, Wall. R. E. Marker, R. B. Wagner, D. P. J. Goldsmith, P. R. Ulshafer, and C. H. Ruof. LXIX. Isolation and structures of thirteen new steroidal sapogenins. New sources for known sapogenins.** R. E. Marker, R. B. Wagner, P. R. Ulshafer, E. L. Wittbecker, D. P. J. Goldsmith, and C. H. Ruof (*J. Amer. Chem. Soc.*, 1943, 65, 1247, 1248, 1248—1249, 1199—1209).—LXVI. The sterol from the seed of *T. foenum-graecum* is diosgenin (I) (cf. Soliman *et al.*, A., 1943, II, 99).

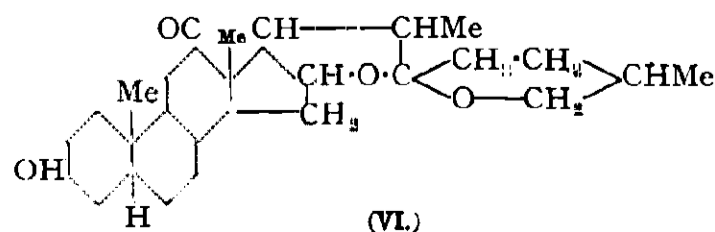
LXVII. (Cf. A., 1943, II, 239.) The sterols from *Beth* root yield (I) (35—60% isolated as acetate), kryptogenin (II) (20—40% isolated as acetate), pennogenin (III),  $\text{C}_{27}\text{H}_{42}\text{O}_4$  (10—20%), m.p.  $247^\circ$ , and small amounts of nologenin (IV),  $\text{C}_{27}\text{H}_{44}\text{O}_5$ , m.p.  $265^\circ$ , unsaturated (diacetate, m.p.  $180^\circ$ ), and fesogenin (V),  $\text{C}_{27}\text{H}_{40}\text{O}_3$ , m.p.  $180^\circ$ , unsaturated. (III) has the structure shown, for it contains 2 OH, no



CO (absorption spectrum), with boiling  $\text{Ac}_2\text{O}$  gives a monoacetate, m.p.  $200^\circ$ , and after prolonged treatment with  $\text{HCl}\cdot\text{EtOH}$  yields (II). (V) contains a conjugated system, since with  $\text{H}_2\text{---}\text{Pd}\cdot\text{BaSO}_4$  it gives a  $\text{H}_2$ -, m.p.  $213^\circ$ , and with  $\text{Na}\cdot\text{EtOH}$  a  $\text{H}_4$ -derivative, m.p.  $240^\circ$ .

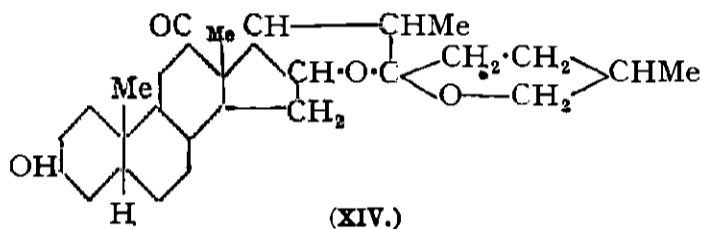
LXVIII. "Nitogenin" (Kon *et al.*, A., 1939, II, 332) from *Balanites aegyptica* is really (I).

LXIX. Isolation of thirteen new sapogenins and new sources of known sapogenins from Mexican and U.S. plants are briefly recorded. Hecogenin (VI),  $\text{C}_{27}\text{H}_{42}\text{O}_4$ , forms, m.p.  $245^\circ$ ,  $253^\circ$ , and  $268^\circ$ , is obtained from 22 plants [1.3% from *Agave toumeyana*, Trel.; 0.7% from *A. gracilipes*, Trel.;  $>0\cdot33\%$  (dry wt. in all cases) from the others]. The structure

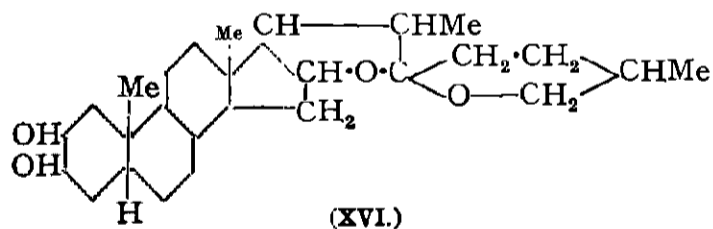


follows from its conversion by boiling  $\text{Ac}_2\text{O}$  into a monoacetate,

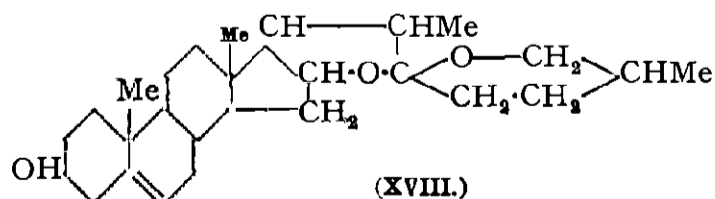
forms, m.p. 243° and 252°, resistance to Clemmensen reduction, formation of a semicarbazone, oxidation by  $\text{CrO}_3$  to *hecogenone* (VII),  $\text{C}_{27}\text{H}_{40}\text{O}_4$ , m.p. 240° (CO at  $\text{C}_{(3)}$ ), and then to *hecogenic acid* (VIII),  $\text{C}_{27}\text{H}_{40}\text{O}_7$ , m.p. 268° (decomp.) (fission between  $\text{C}_{(2)}$  and  $\text{C}_{(3)}$ ); Me<sub>2</sub> ester, m.p. 187°, and Wolff-Kishner reduction to tigogenin. *Manogengen* (IX),  $\text{C}_{27}\text{H}_{42}\text{O}_5$ , forms, m.p. 241—243°, 254°, and 264° (diacetate, forms, m.p. 215°, 242°, and 255°), is isolated from 25 plants [abundantly in *Manfreda maculosa*, Hook; 0.53% from *A. huachucensis*, Baker; >0.17% from other plants]; it is the 2-OH-derivative of (VI), since with  $\text{CrO}_3$  it gives (VIII) and by Wolff-Kishner reduction gives gitogenin (X). *Yucca schottii*, Engelm., *Y. elata*, Engelm., and *Y. flaccida*, Haw., yield *yuccagenin* (XI),  $\text{C}_{27}\text{H}_{42}\text{O}_4$ , forms, m.p. 246° and 252° (diacetate, m.p. 178°), which with  $\text{H}_2$ -PtO<sub>2</sub> and a little AcOH in Et<sub>2</sub>O gives (X), with  $\text{H}_2\text{O}_2$  gives a tetraol,  $\text{C}_{27}\text{H}_{44}\text{O}_6$ , m.p. 350° [with  $\text{CrO}_3$ -AcOH and then, after dehydration, Zn-AcOH gives chlorogenic acid], and is thus the  $\Delta^5:6$ -derivative of (X). *Y. brevifolia*, Engelm., *Y. harrimanii*, Trel., and *Samuela carnerosana*, Trel., contain *kammogenin* (XII),  $\text{C}_{27}\text{H}_{40}\text{O}_5$ , m.p. 242° [diacetate, forms, m.p. 243° and 260°; also present in the mother-liquors from (XI) obtained from *Y. schottii*], which gives a semicarbazone but resists Clemmensen reduction, gives (XI) by Wolff-Kishner reduction, is hydrogenated (PtO<sub>2</sub>; Et<sub>2</sub>O + a little AcOH) as diacetate to the diacetate of (IX), and is thus the 12-CO derivative of (XI). *Rockogenin*,  $\text{C}_{27}\text{H}_{44}\text{O}_4$ , m.p. 221° (acetate, m.p. 206°), is isolated with much (VI) from *A. gracilipes*, Trel.; it is 12-dihydrohecogenin, being obtained from (VI) by  $\text{H}_2$ -PtO<sub>2</sub> or Na-EtOH and oxidised to (VII) by  $\text{CrO}_3$ -AcOH. The saponins from *A. huachucensis*, Baker (1360 kg.), yield (IX) (22%), (X) (50%), (VI) (22%), and *agavogenin* (XIII) (5%),  $\text{C}_{27}\text{H}_{44}\text{O}_5$ , m.p. 242° (triacetate, m.p. 228°). (XIII) is 12-dihydromanogengenin, being obtained from (IX) by  $\text{H}_2$ -PtO<sub>2</sub> or Na-EtOH and oxidised by  $\text{CrO}_3$  to (VIII). *Furcogenin* (XIV),  $\text{C}_{27}\text{H}_{42}\text{O}_4$ , m.p. 225°, is obtained from *Furcraea sellosa* and, with much smilagenin (XV) and little (XI), from *Y. flaccida*, Haw. It has the  $\beta$ -configuration at  $\text{C}_{(3)}$ , giving a ppt. with digitonin in EtOH. It gives a monoacetate, m.p. 225°, is reduced (Wolff-Kishner) to (XV), but resists Clemmensen reduction, and thus has the formula shown. *Samuela carnerosana*, Trel., and *Y. schottii*,



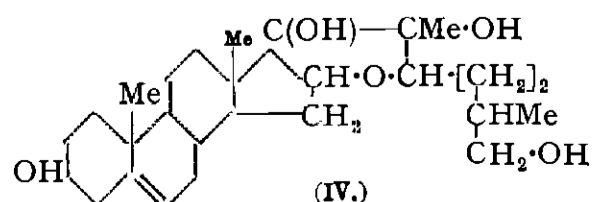
Engel., contain *samogenin* (XVI),  $\text{C}_{27}\text{H}_{44}\text{O}_4$ , m.p. 210—212° (diacetate, m.p. 195—198°; digitonide), and *mexogenin* (XVII),  $\text{C}_{27}\text{H}_{42}\text{O}_5$ , m.p. 246° (diacetate, m.p. 208°). (XVI) is unaffected by boiling HCl-EtOH, is converted by NaOEt at 200° into *episamogenin* ( $\alpha$ -configuration at  $\text{C}_{(3)}$ ), m.p. 235—237°, and is oxidised by  $\text{CrO}_3$ -AcOH to *samogenic acid*, m.p. 264° (decomp.), isomeric with gitogenic acid; the reactions indicate the structure shown. (XVII) gives a semi-



carbazone but resists Clemmensen reduction, by Wolff-Kishner reduction gives (XVI), and is thus the 12-CO-derivative of (XVI). *Dioscorea testudinaria* and 12 other plants yield (I) and *yamogenin* (XVIII),  $\text{C}_{27}\text{H}_{42}\text{O}_3$ , m.p. 200—201° (acetate, m.p. 180—182°); this yields (I) by isomerisation of the side-chain, is hydrogenated as acetate in Et<sub>2</sub>O + AcOH to neotigogenin acetate, and thus has the structure shown. The saponins from *Y. schottii* (1364 kg.) yield

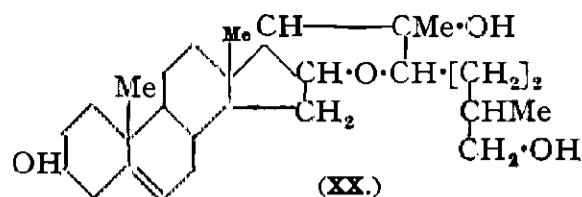


(XI) (59%), (XV) (13%), (XII) (13%), (XVI) (8%), (X) (2%), (XVII) (1%), and *texogenin* (XIX) (4%),  $\text{C}_{27}\text{H}_{44}\text{O}_4$ , m.p. 171—172° (diacetate, m.p. 170—172°). (XIX) is converted into (XVI) by boiling HCl-EtOH and is thus the  $\text{C}_{(22)}$ -epimeride of (XVI). The annexed structure is suggested for (IV), since it contains 4 OH, with boiling



$\text{Ac}_2\text{O}$  gives a diacetate, m.p. 200° (Part LXVII, m.p. 180°), and in boiling HCl-EtOH gives (III) and then (II). The mother-liquor

from (IV) (from *Beth* root) yields *kappogenin* (XX),  $\text{C}_{27}\text{H}_{44}\text{O}_4$ , m.p. 230°, the structure of which is proved because it possesses 3 OH, gives a diacetate, m.p. 178°, with boiling 2N-HCl-EtOH gives (I), and



with  $\text{CrO}_3$  at 25°, followed by hydrolysis, gives  $\Delta^5:16$ -pregnadien-3( $\beta$ )-ol-20-one. Sarsasapogenin is isolated from 26 (1% from *Y. elata*, Engelm.), (XV) from 28 (0.8% from *Y. flaccida*, Haw.; 0.75% from *A. lophantha*), (X) from 16 (1—1.1% in *A. schottii*, *Y. filamentosa*, L., and *Manfreda virginica*, L.), chlorogenin from 2, tigogenin from 10 (0.88% from *Y. whipplei typica*), (I) from 29, (II) from 12, and sitosterol from 18 new sources (0.14% from *Y. arizonica*, McKel.).

R. S. C.

Steroid glucuronide, m.p. 267—269°, from human urine [steroid, m.p. 212—213° (corr.) (acetate, m.p. 192—194°; oxime, m.p. 223—225°)].—See A., 1943, III, 656.

## V.—TERPENES AND TRITERPENOID SAPOGENINS.

**Unambiguous synthesis of camphor. I. Synthesis of camphononic acid.** N. C. Ganguly (*J. Indian Chem. Soc.*, 1943, 20, 101—104).— $\text{CMe}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  (100 g.), condensed with  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  in AcOH- $\text{NH}_2\text{Ac}$ , gives *Et*  $\alpha$ -cyano- $\beta\gamma\gamma$ -trimethylglutaconate, b.p. 145°/4 mm., which adds HCN to give *Et*  $\alpha\beta$ -dicyano- $\beta\gamma\gamma$ -trimethylglutarate, b.p. 170°/5 mm. Boiling for 30 hr. with 72%  $\text{H}_2\text{SO}_4$  hydrolyses this to 20 g. of camphoronic acid, m.p. 168°. Me<sub>3</sub> camphoronate (b.p. 134°/3 mm.), obtained using  $\text{CH}_2\text{N}_2$ , is partly hydrolysed (on the primary  $\text{CO}_2\text{Me}$ ) by NaOH-MeOH; the mono-acid is then converted into its chloride by  $\text{SOCl}_2$  in  $\text{C}_6\text{H}_6$  in presence of  $\text{C}_5\text{H}_5\text{N}$ . Following the technique of Bachmann *et al.* (A., 1940, II, 225), the acid chloride in  $\text{C}_6\text{H}_6$  is treated successively with  $\text{CH}_2\text{N}_2$  in Et<sub>2</sub>O and  $\text{Ag}_2\text{O}$  in MeOH, thus giving Me<sub>3</sub> homocamphoronate, b.p. 150°/5 mm. This with Na dust and a trace of EtOH in  $\text{C}_6\text{H}_6$  gives Me<sub>2</sub> 2:2:3-trimethylcyclopentanone-3:5-dicarboxylate, b.p. 157°/9—10 mm., which, when refluxed for 20 hr. with 20%  $\text{H}_2\text{SO}_4$ , gives camphononic acid, m.p. 230—231° (lit. 232°) [oxime, m.p. 189—190° (lit. 186—187°); Et ester, b.p. 106—110°/8 mm.]. S. A. M.

**Synthesis of *dl*-pinonic acid.** F. L. N. Rao (*J. Indian Chem. Soc.*, 1943, 20, 97—100).—*trans*-Pinic acid (for synthesis cf. A., 1937, II, 377) is converted into *trans*-1-carbethoxy-2:2-dimethylcyclobutane-3-acetyl chloride (A., 1938, II, 283, 412), which, with  $\text{NHPh}_2$  in  $\text{C}_5\text{H}_5\text{N}$ , gives the -3-acetdiphenylamide, m.p. 99—100°. 95%  $\text{H}_2\text{SO}_4$ , at 60—65°, gives the corresponding -1-carboxy-compound (m.p. 139—140°), the acid chloride of which (prepared by using  $\text{SOCl}_2$ ) with  $\text{CdMeCl}$  in Et<sub>2</sub>O gives *trans*-*dl*-pinondiphenylamide (yield 30%) (semicarbazone, m.p. 204—205°, undepressed by adding a sample, m.p. 205—206°, prepared from pinonic acid). Boiling MeOH-KOH gives *dl*-pinonic acid, m.p. 103—105°. S. A. M.

**Attempted preparation of a tetracyclic hydrocarbon of the camphane series.** M. Lipp (née Bredt-Savelsberg) [with N. Proth] (*Ber.*, 1941, 74, [B], 1—6).—2-Aminocyclocamphane (I), b.p. 125—132°/12 mm. (phenylcarbamidocyclocamphane, no m.p., sublimes ~150°), is obtained by reduction ( $\text{Na} + \text{C}_5\text{H}_{11}\text{OH}$ ) of cyclocamphanoneoxime.

The hydrochloride of (I), KOH, and excess of  $\text{ClCO}_2\text{Et}$  afford the urethane (II), b.p. 142°/9 mm.,  $[\alpha]_D^{20} -3.06^\circ$  in EtOH. Because of the instability of the NO-compound obtained when (II) is treated with dry  $\text{N}_2\text{O}_3$  in Et<sub>2</sub>O at  $<-20^\circ$ , the dried solution is used directly. NaOMe (excess) at  $-20^\circ$  affords: (i) not quite pure cyclocamphanyl Me ether (III), b.p. 64°/12 mm.; (ii)  $\text{C}_{10}\text{H}_{16}\text{O}$  (IV), sublimes at 82—84°, m.p. (not sharp) 160—163°,  $[\alpha]_D^{20} +27.72^\circ$ ; (iii) unchanged (II). When MeOH-free NaOMe is used (III) is not formed. (IV) gives an inhomogeneous 3:5-dinitrobenzoate (different fractions, m.p. 126—134°). (IV) with  $\text{CrO}_3$  gives cyclocamphane-2-one and is a mixture of cyclocamphan-2-ol (3:5-dinitrobenzoate, m.p. 138°) and its epimeride. The formation of these products is attributed to the production from the nitroso-urethane of a diazotate, instead of a diazo-compound, which loses  $\text{N}_2$  to give the Na-derivative of (IV) and reacts with MeOH to give (III). J. WA.

**isoAlcohols of the camphane series. II. 2-isoHydroxycyclocamphane.** M. Lipp (née Bredt-Savelsberg) [with E. Oeckinghaus and C. L. Conze] (*Ber.*, 1941, 74, [B], 6—12; cf. A., 1935, 496).—Hydrogenations are carried out in a Au-plated steel autoclave. Camphor is completely reduced ( $\text{H}_2$ -Pt-black-AcOH) at 40—50 atm. and room temp. to 20% of isobornyl acetate and 80% of isoborneol (3:5-dinitrobenzoate, m.p. 139°; previously recorded m.p. 133° is a misprint; A., 1931, 1068). Camphor and epicamphor reduced in methylcyclohexane (I) give respectively isoborneol and

>90% of epi-isobornyl 3:5-dinitrobenzoate, m.p. 118—119°. cyclo-Camphan-2-one, purified through the semicarbazone, reduced in (I) gives iso-cyclocamphanol 3:5-dinitrobenzoate, m.p. 112—113° (Kofler micro-m.p. 116°),  $[\alpha]_D^{25} -75.65^\circ$  in PhMe (additive compound with  $\alpha\text{-C}_{10}\text{H}_{17}\cdot\text{NH}_2$ , m.p. 163—164°). iso-cyclocamphanol, m.p. 180—181°,  $[\alpha]_D^{19} -36.07^\circ$  in  $\text{C}_6\text{H}_6$ , as Na-derivative, undergoes inversion at 230° in  $\text{C}_6\text{H}_6$  to cyclocamphanol (3:5-dinitrobenzoate, m.p. 138—139°). J. WA.

**$\omega$ -Benzoylcamphene.** Y. Asahina and T. Sano (*Ber.*, 1940, 73, [B], 747—753).—Data of Lipp *et al.* (A., 1927, 883; 1929, 1308) are modified and extended. The product (I), b.p. 145—150°/4 mm., obtained from  $\omega$ -benzoylborneol by  $\text{KHSO}_4$  at 180—190°, consists mainly of  $\omega$ -benzoylcamphene (II) with a little  $\omega$ -benzoyltricycylene (III). It gives a small amount of the semicarbazone (IV), m.p. 210—211°, of (III). With  $\text{KMnO}_4$  in  $\text{COMe}_2$ , (I) gives BzOH, camphenilone, and a little (III), m.p. 59—60°, b.p.  $\sim 115^\circ/5$  mm. [semicarbazone = (IV)]. MgPhBr in boiling  $\text{Et}_2\text{O}$ , followed by aq.  $\text{NH}_4\text{Cl}$ , converts (III) into  $\alpha\alpha$ -diphenyl- $\beta$ -tricyclenylethylene (V), m.p. 70—71°, b.p.  $\sim 154^\circ/0.06$  mm. With MgPhBr in boiling  $\text{Et}_2\text{O}$ , (I) gives the diphenylcarbinol,  $\text{C}_{23}\text{H}_{26}\text{O}$ , b.p. 174°/0.06 mm., dehydrated by twice boiling with  $\text{Ac}_2\text{O}$  into a (? mixed) hydrocarbon,  $\text{C}_{23}\text{H}_{24}$ , b.p. 172—173°/0.08 mm., which with  $\text{O}_3$  in  $\text{CHCl}_3$  gives tricyclenic acid,  $\text{C}_{10}\text{H}_{14}\text{O}_2$ , sinters 149°, m.p. 151°, and  $\text{COPh}_2$ , and with  $\text{KMnO}_4$  in  $\text{COMe}_2$  gives much (V) and substances,  $\text{C}_{23}\text{H}_{26}\text{O}_2$ , m.p. 160°, and  $\text{C}_{23}\text{H}_{24}\text{O}_3$ , m.p. 196—198°, and an acid,  $\text{C}_{10}\text{H}_{16}\text{O}_3$ , m.p. 190—192°. Camphenylideneacetone nitrile (VI), b.p. 128°/14 mm., with MgPhBr in boiling  $\text{Et}_2\text{O}$  and then aq.  $\text{NH}_4\text{Cl}$  gives (II), b.p. 125—127°/0.03 mm. [containing a little (III), present in (VI)], which with  $\text{KMnO}_4$  or MgPhBr (and then  $\text{O}_3$  or  $\text{KMnO}_4$ ) gives the same products as does (I). No hydrocarbon,  $\text{C}_{23}\text{H}_{24}$ , m.p. 83—84°, could be obtained. R. S. C.

**Cafesterol.** II. P. N. Chakravorty, (Miss) M. M. Wesner, and R. H. Levin (*J. Amer. Chem. Soc.*, 1943, 65, 929—932; cf. A., 1943, II, 40).—Cafesterol (I) which is probably diterpenoid (prep. described), has m.p. 147—151°,  $[\alpha]_D^{30} -156^\circ$  in  $\text{CHCl}_3$ ; the solution darkens and  $[\alpha]$  becomes  $-161^\circ$  in 2 weeks. The acetate, m.p. 162—165° (160—165°) [absorption max. at 290  $\mu$ . ( $\epsilon$  6300, decreases on irradiation)], with  $\text{H}_2$ -Pd-C in  $\text{EtOH}$  at 34 lb. gives tetrahydrocafesteryl acetate (II), m.p. 152—154.5°,  $[\alpha]_D^{29} -20.4^\circ$  in  $\text{CHCl}_3$ , and thence tetrahydrocafesteryl (III), m.p. 154.5—157° (cf. Wettstein *et al.*, A., 1942, II, 198, 371).  $(\text{CH}\cdot\text{CO})_2\text{O}$  combines with (I) in  $\text{C}_6\text{H}_6$  at 35—40° in 0.5 hr. or slowly at room temp. to give the adduct,  $\text{C}_{24}\text{H}_{30}\text{O}_6$ , m.p. 190—192°,  $[\alpha]_D^{29} -43^\circ$  in  $\text{COMe}_2$ , wherefore (I) contains  $\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{C}$ . With Zn dust at 180—200°/1.5 mm. (20 min.), followed by distillation at 0.02 mm., (II) gives oxcafestanaldehyde,  $\text{C}_{18}\text{H}_{28}\text{O} > \text{CH}\cdot\text{CHO}$ , amorphous (semicarbazone, m.p. 217—218°; p-nitrophenylhydrazone, m.p. 231—233°), converted by  $\text{KMnO}_4$ - $\text{COMe}_2$  into oxcafestanic acid (IV), m.p. 260—262°,  $[\alpha]_D^{30} -39.7^\circ$  in  $\text{CHCl}_3$  (Me ester, m.p. 123.5—124.5°), which is unaffected by  $\text{H}_2$ -PtO<sub>2</sub>-HCl-AcOH at 60°/50 lb. (I) and (III) are oestrogenic (Kahnt-Doisy) in 2-mg. doses. In 20-mg. doses (IV) has no cortin activity (Ingle) and contains <1 oestrogenic rat unit per 5 mg. R. S. C.

**Cafesterol.** III. isoCafesterol. P. N. Chakravorty, R. H. Levin, (Miss) M. M. Wesner, and G. Reed (*J. Amer. Chem. Soc.*, 1943, 65, 1325—1328; cf. *supra*).—Adding Na to cafesterol (I) in boiling  $\text{EtOH}$  gives isocafesterol (II), m.p. 156—159° [not depressed by (I)],  $[\alpha]_D^{30} -108^\circ$  in  $\text{CHCl}_3$ ,  $-114^\circ$  in  $\text{COMe}_2$  [acetate (III), m.p. 163—167°, not depressed by the acetate of (I)]. (I) absorbs 2 and (II) absorbs 2.5 O from  $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  in  $\text{Et}_2\text{O}$ ; both absorb 8 Br; in presence of Pd-C in  $\text{EtOH}$  they give the same  $\text{H}_4$ -derivative. With  $(\text{CH}\cdot\text{CO})_2\text{O}$  in warm  $\text{C}_6\text{H}_6$ , (II) gives an adduct, m.p. 177—180° (decomp.),  $[\alpha]_D^{30} -45^\circ$  in  $\text{COMe}_2$ , converted into (III) by  $\text{Ac}_2\text{O}\text{-C}_5\text{H}_5\text{N}$ , and regenerating (II) at 130—160°/0.01 mm.; the adduct from (I) similarly regenerates (I) at 125—145°/0.008 mm., so that the adducts also differ. Boiling  $\text{NaOMe}\text{-MeOH}$  does not convert (I) into (II). In conc. HCl, (I) gives a blue and (II) a pink colour, so that acid does not reverse the change. In  $\text{Pr}^\text{iso}\text{OH}$ , (I) has an absorption max. at 292  $\mu$ . ( $\epsilon \sim 6500$ ) and (II) at 226  $\mu$ . ( $\epsilon \sim 8300$ ); thus the ethylenic linkings in (I), but not in (II), are probably in the same ring; partial structures are suggested. R. S. C.

**Rubber, polyisoprenes, and allied compounds.** IV. Relative tendencies towards substitutive and additive reaction during chlorination.—See A., 1943, II, 289.

**Constitution of l-pimaric acid.** W. Sandermann (*Ber.*, 1941, 74, [B], 154—161).—A mixture of pine rosin acid [crude l-pimaric acid (I)] and  $(\text{C}\cdot\text{CO}_2\text{Me})_2$  (II) in  $\text{Et}_2\text{O}$  has  $[\alpha]_D -75^\circ \rightarrow +87.5^\circ$  (const.) in 46 hr., indicating, together with the absorption spectrum of (I), that the two double linkings of (I) are in the same ring. (I) and (II) at 180° afford no volatile unsaturated hydrocarbon and the adduct gives no definite product with Pd-C at 300°, whilst (I) alone gives 80% of retene. The "residual acid," m.p. 162—168°,  $[\alpha]_D +55^\circ$  in  $\text{Et}_2\text{O}$ , is obtained from crude (I) after removal of (I) as the

benzoquinone adduct and contains 50% of d-pimaric acid, abietic acid, and "proabietic" acid. J. WA.

## VI.—HETEROCYCLIC.

**Tetrahydrofurfuryl ethers etc.**—See B., 1943, II, 283.

**3-Chloro-2-ethoxy-2-methyltetrahydrofuran.**—See B., 1943, II, 277.

**Condensation of pyromucic acid with N-methylolamides.** R. O. Cinnéide (*Proc. Roy. Irish Acad.*, 1943, 49, B, 143—150).—Pyromucic acid and  $\text{OH}\cdot\text{CH}_2\cdot\text{NHBz}$  in conc.  $\text{H}_2\text{SO}_4$  give 5-N-benzamidomethylfuran-2-carboxylic acid (I), m.p. 168—169.5° and 191—192° (two forms) (Et ester: labile m.p. 95—96°; stable m.p. 125—127°). Oxidation of (I) with  $\text{K}_3\text{Fe}(\text{CN})_6$  gives furan-2:5-dicarboxylic acid; (I) with boiling  $\text{HgCl}_2\text{-H}_2\text{O}$  (or  $\text{H}_2\text{O}$  at 150—170° in sealed tube) gives 2-benzamidomethylfuran (II) and tetra(chloromercuri)furan. The Na salt of (I) with boiling  $\text{HgCl}_2\text{-H}_2\text{O}$  yields 5-benzamidomethyl-2-chloromercurifuran, m.p. 162—164°, which with boiling aq. HCl gives (II). Pyromucic acid and  $\text{OH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me-p}$  (prep. described) give 5-p-toluamidomethylfuran-2-carboxylic acid (III), m.p. 195—198°, which reacts like (II) with  $\text{HgCl}_2\text{-H}_2\text{O}$  on heating in a sealed tube. Pyromucic acid and o-nitrobenzhydroxymethylamide, m.p. 114—117° (prep. described), give 5-N-o-nitrobenzamidomethylfuran-2-carboxylic acid (IV), m.p. 195—198°, which reacts like (I). Preps. of 2-p-tolu-, m.p. 102°, 2-benz-, m.p. 101—102°, and 2-o-nitrobenz-amidomethylfuran, m.p. 107—108°, are also given. J. H. BA.

**Pyrones and related compounds.** II. New reaction product of acetonedicarboxylic acid and acetic anhydride. R. Kaushal, P. B. Bhishe, and S. S. Deshapande (*J. Indian Chem. Soc.*, 1943, 20, 51—53).— $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$  is converted by  $\text{Ac}_2\text{O}$  into 2:6-dihydroxy-1:4-pyrone and 3'-keto-6-methyl-3':4'-dihydrocyclobutadieno-1':2'-2:3-1:4-pyrone-5-carboxylic acid (I), m.p. 157° ( $\text{NH}_2\text{Ph}$  salt, m.p. 185°). If a considerable excess of  $\text{Ac}_2\text{O}$  is used (I) is the sole product. Its structure is confirmed by its production from  $\text{Ac}_2\text{O}$  and dehydracetocarboxylic acid. H. W.

**Action of acids on 2:3-epoxy-2:3-diphenylindanone.**—See A., 1943, II, 266.

**Structural chemistry of naturally occurring flavones and flavonols.** P. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1943, 17, A, 119—141).—An account of the chemistry of the members of the group. H. W.

**Isomorphous replacement of bivalent atoms and  $\psi$ -atoms [groups] in organic compounds.** G. Bruni (*Ber.*, 1940, 73, [B], 763—764).—The work of Lüttringhaus *et al.* (A., 1940, II, 305) and Rheinboldt *et al.* (A., 1943, II, 263) was anticipated on a much wider scale by Garelli *et al.* (A., 1894, i, 157; 1895, ii, 205) and Bruni (*Ahrens Sammlung*, 1901, 6, 415), whose results are briefly recapitulated. R. S. C.

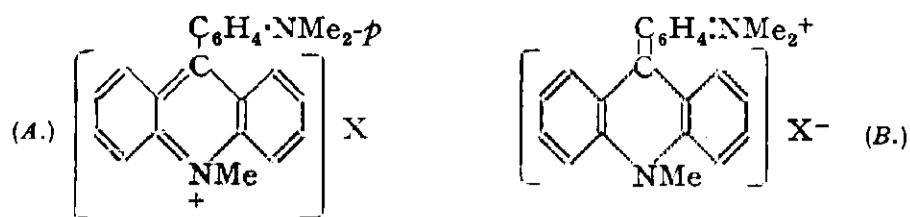
**Rubrofusarin,  $\text{C}_{15}\text{H}_{12}\text{O}_5$ .**—See A., 1943, III, 600.

**Esters of 1:4-dioxan-2:3-diol.**—See B., 1943, II, 277.

**Action of alkalis on substituted benzodioxins.** H. Irving and E. G. Curtis (*J.C.S.*, 1943, 319—321).—8-Nitro-6-methyl-2:4-bis(trichloromethyl)-1:3-benzodioxin (I), m.p. 175—176°, is prepared from 3:1:4- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$  and chloral hydrate in conc.  $\text{H}_2\text{SO}_4$ . It is unaffected by  $\text{EtOH-KOAc}$  but  $\text{EtOH-KOH}$  opens the hetero ring, giving 5-nitro-4-ethoxy-m-toluic acid (II), m.p. 148—149°. 7-Nitro-6-methyl-2:4-bis(trichloromethyl)-1:3-benzodioxin, m.p. 143°, gives the 2:4-bis(dichloromethylene) compound, m.p. 101°, with  $\text{EtOH-KOH}$ . (I) with  $\text{SnCl}_2$  in  $\text{Ac}_2\text{O-AcOH-HCl}$  gives 8-amino-6-methyl-2:4-bis(trichloromethyl)-1:3-benzodioxin, m.p. 140° (Ac derivative, m.p. 171.5°), which with  $\text{EtOH-KOH}$  gives the 2:4-bis(dichloromethylene) compound, m.p. 121° (Ac derivative, m.p. 201°). 5:7-Dichloro-6-methoxy-2:4-bis(trichloromethyl)-1:3-benzodioxin, m.p. 189—190° (from the OH-derivative and  $\text{Me}_2\text{SO}_4\text{-aq. KOH}$ ), gives the 2:4-bis(dichloromethylene) derivative, m.p. 114.5°, with  $\text{EtOH-KOH}$ . 6-p-Tolueneazo-2:4-bis(trichloromethyl)-1:3-benzodioxin with  $\text{EtOH-KOH}$  also gives the 2:4-bis(dichloromethylene) derivative, m.p. 147—148°. Di-(6-nitrobenzodioxinyl)-8:8'-ketone with aq. NaOH gives  $\text{CH}_2\text{O}$  and 5:5'-dinitro-2:2'-dihydroxy-3:3'-bis(hydroxymethyl)benzophenone, m.p. 260° (phenylhydrazone, m.p. 226—227°). These results confirm the mechanisms previously (A., 1934, 531) proposed. 4:1:3-OEt $\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{Et}$  [from 4:1:3-OH $\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{H}$  (III),  $\text{Et}_2\text{SO}_4$ , and  $\text{K}_2\text{CO}_3$  in  $\text{COMe}_2$  or from the Et ester of (III),  $\text{EtBr}$ , and  $\text{NaOEt}$ ] is hydrolysed (aq.  $\text{EtOH-KOH}$ ) to the acid, m.p. 76—78°, which is nitrated to (II). Nitration of (III) gives the 5- $\text{NO}_2$ -derivative, new m.p. 176—177°, decarboxylated (boiling quinoline) to 3:1:4- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$ . J. H. BA.

**Condensation of phosphorus oxychloride-acridone with dimethylaniline.** K. Gleu and A. Schubert (*Ber.*, 1940, 73, [B], 757—761).—Acridones and  $\text{POCl}_3$  give compounds,  $[o\text{-C}_6\text{H}_4\langle\text{CCl}\rangle\text{C}_6\text{H}_4\text{-o}]\text{PO}_2\text{Cl}_2$ , in which the Cl at  $\text{C}_{10}$  is very reactive. Thus, melting 10-methyl-

acridone,  $\text{POCl}_3$ , and  $\text{NPhMe}_2$  gives a blue melt (A) ( $\text{X} = \text{PO}_2\text{Cl}_2$ ), which in ice gives the carbinol, converted by boiling  $\text{MeOH}$  into



5-methoxy-10-methyl-5,10-dihydroacridine (I), m.p. 170°. The OMe in (I) is mobile, for, with boiling  $\text{EtOH}$ , (I) gives 5-ethoxy-, m.p. 139°, with dil.  $\text{HCl}$  and then  $\text{NaOH}$  gives impure 5-hydroxy- (II), m.p. 129°, unstable, and with 13N-aq.  $\text{NH}_3$  gives 5-amino-, m.p. 146°, 5-p-dimethylaminophenyl-10-methyl-5,10-dihydroacridine. Treating (I) with 2N- $\text{HCl}$  and then with  $\text{NaOH}$  until pptn. of (II) begins, heating at 60°, and saturating with  $\text{NaCl}$  yields the blue 5-p-dimethylaminophenyl-10-methylacridinium chloride ( $\text{A} \rightleftharpoons \text{B}$ ) ( $\text{X} = \text{Cl}$ ) + 2.5 $\text{H}_2\text{O}$ , which in an excess of mineral acid gives pale yellow, non-resonating, sol. salts in which both N are combined with acid; a nitrate,  $[\text{C}_{22}\text{H}_{21}\text{N}_2]\text{NO}_3 \cdot 2\text{HNO}_3$ , is isolated. 10-Phenylacridone similarly yields 5-methoxy-, m.p. 210—211°, 5-ethoxy-, m.p. 154°, and 5-amino-, m.p. 181°, 10-phenyl-5-p-dimethylaminophenyl-5,10-dihydroacridine, and a blue acridinium chloride. R. S. C.

**Interaction of phosphorus oxychloride-acridone with Grignard reagents.** K. Gleu and A. Schubert (*Ber.*, 1940, 73, [B], 805—811).—The compound obtained from acridone and  $\text{POCl}_3$  with  $\text{MgPhBr}$  in  $\text{Et}_2\text{O}$  gives  $\text{PPh}_2\text{O}_2\text{H}$ , 5 : 5'-diacridyl, and  $\text{Ph}_2$ . With 10-substituted acridones further reduction occurs. Thus, 10-methyl- or 10-phenyl-acridone gives 10 : 10'-dimethyl- or 10 : 10'-diphenyl-5 : 5'-diacridylidene with, after treatment with  $\text{HNO}_3$ , 10 : 10'-dimethyl- or 10 : 10'-diphenyl-diacridylum dinitrate. R. S. C.

**Diketopyrazolidines.** H. Rühkopf (*Ber.*, 1940, 73, [B], 820—822).—Diketopyrazolidines are obtained from (a)  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (excess),  $\text{CR}_2(\text{CO}_2\text{Et})_2$  ( $\text{R} = \text{H}$ , alkyl, or aryl), (b)  $\text{NHPh} \cdot \text{NH}_2$ ,  $\text{CR}_2(\text{CO}_2\text{Et})_2$  ( $\text{R} = \text{H}$  or alkyl, not aryl), or (c)  $(\text{NHPh})_2$ ,  $\text{CH}_2(\text{CO}_2\text{Et})_2$  (not its derivatives), and, in all cases,  $\text{NaOEt}$  in  $\text{EtOH}$  at 180—200°. The products containing no, or one, substituent on N are acetylated by boiling  $\text{Ac}_2\text{O}$ , but di-N-substituted products are unaffected. Thus are prepared 3 : 5-diketo-4 : 4-diethyl- (90%), m.p. 270° (lit. 256°, 260—261°), -4 : 4-di-n-propyl- (70%), m.p. 256° [some  $\text{CPr}^a_2(\text{CO}_2\text{H})_2$  is also formed], -4-phenyl-4-ethyl- (I) (70%), m.p. 198° (3-O-Ac derivative, m.p. 159.5°), -4-ethyl-4-n-propyl- (70%), m.p. 232.5°, -4 : 4-diallyl- (70%), m.p. 280°, and -1 : 2-diphenyl- (90%), m.p. 173.5°, -1 : 2-pyrazolidine. These products are fairly sol. in  $\text{H}_2\text{O}$  and stable to acid and alkali (e.g., boiling 50%  $\text{KOH}$  for 50 hr. or autoclaving at 10 atm.); they have no, or a weakly acid, taste, never a bitter one, and resemble pyrazolones in physiological action but have no advantage thereover. With  $\text{Br}$  in hot  $\text{AcOH}$ , (I) gives 3 : 5-diketo-1 : 2-phenylethylmalonyl-4-phenyl-4-ethylpyrazolidine (40%),  $\text{CPhEt} \begin{smallmatrix} \text{CO} \cdot \text{N} \cdot \text{CO} \\ \text{CO} \cdot \text{N} \cdot \text{CO} \end{smallmatrix} \text{CPhEt}$ , m.p. 238°, and some  $\text{CPhEt}(\text{CO}_2\text{H})_2$ . R. S. C.

**Bacterial inhibition by metabolite analogues.** V. Reactions and antibacterial properties of p-diazine di-N-oxides. H. McIlwain (*J.C.S.*, 1943, 322—325).—The di-N-oxides of the following have been prepared by treatment of the appropriate base in  $\text{AcOH}$  with 100-vol.  $\text{H}_2\text{O}_2$ : quinoxaline, m.p. 238—239°, 2-methylquinoxaline (I), m.p. 180—181°, 2-methyl-3-n-amyloquinoxaline, m.p. 107°, and 1 : 2 : 3 : 4-tetrahydrophenazine, m.p. 188°. Iodinin [di-N-oxide of the dihydroxyphenazine obtained from *Chromobacterium iodinum* (cf. Clemo *et al.*, A., 1938, II, 248)] could only be prepared using  $\text{BzO}_2\text{H} \cdot \text{C}_6\text{H}_6$ . The oxides retain the basic characters of the diazines, but those with saturated 2-substituents have also acidic properties, explained as due to tautomeric oxime forms. (I) changes in alkali to a blue product, the conversion being accelerated by light. Two quinoxaline di-N-oxides characterised by unsubstituted 2-positions react with keto-methylene compounds in dil. alkaline solution. All the di-N-oxides are readily reduced to the diazines, whilst quinoxalines, but not phenazines, undergo further fission ( $\text{Zn} \cdot \text{H}_2\text{SO}_4$ ) to  $\sigma\text{-C}_6\text{H}_4(\text{NH}_2)_2$  and monoketones. All the di-N-oxides are inhibitory to bacterial growth in concns. in which their parent diazines are inactive. F. R. S.

**Preparation and cleavage of d-arabo-tetrahydroxybutylquinoxaline.** H. Ohle and M. Hielscher (*Ber.*, 1941, 74, [B], 13—17; cf. A., 1934, 392).—Optimal conditions for the prep. of 3-d-arabo-tetrahydroxybutylquinoxaline (I) from fructose (62% yield) are given. Glucose and mannose give only 35% yields. Cleavage of (I) with 5 mols. of  $\text{NHPh} \cdot \text{NH}_2$  in boiling  $\text{H}_2\text{O}$  ( $\text{H}_2$  atm.) proceeds slowly, giving a ppt. of quinoxaline-3-aldehydephenylhydrazone (II) (9%), m.p. 234°,  $\text{NH}_3$  (18.4%), unchanged (I) (73%), and  $\text{NH}_2\text{Ph}$  (11%). Cleavage in alkaline solution shows that 2.79 mols. of  $\text{NHPh} \cdot \text{NH}_2$  are consumed per mol. of (I), but no  $\text{H}_2\text{O}$ -insol. material is produced. Cleavage in boiling dil.  $\text{AcOH}$  ( $\text{H}_2$  atm.) gives unchanged (I) (60%) and a compound,  $\text{C}_{18}\text{H}_{16}\text{O}_3\text{N}_4$  (III) (29.5%), m.p. 218°,  $[\alpha]_D^{25} -19.1^\circ$

in  $\text{C}_5\text{H}_5\text{N}$ ; repetition on a large scale gives a small amount of (II). (III) with  $\text{Ac}_2\text{O} \cdot \text{C}_5\text{H}_5\text{N}$  gives a triacetate, m.p. 123—124°,  $[\alpha]_D^{25} +81.5^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ ,  $[\alpha]_D^{21} +64.4^\circ$  in  $\text{CHCl}_3$ . Catalytic deacetylation (Zemplén) regenerates (III), which thus retains the side-chain of (I). J. W. A.

**New syntheses of heterocyclic compounds. II. 2-Phenyl-3 : 4 : 6 : 7-dibenzo-1 : 5-naphthyridine.** V. A. Petrow, M. V. Stack, and W. R. Wragg (*J.C.S.*, 1943, 316—318).—2-(o-Benzamidophenyl)pyridine (I), m.p. 117° [picrate, m.p. 155° (decomp.)], is obtained from the corresponding  $\text{NH}_2$ -compound [picrate, m.p. 185—186° (decomp.)], and the 3-o-derivative (II), m.p. 132° [picrate, m.p. 168° (decomp.)], is similarly prepared from the  $\text{NH}_2$ -compound [picrate, m.p. 164° (decomp.)]. 2-Amino- furnishes 2-acetamido-3-phenylquinoline (III), m.p. 107—108°. 2-(o-Benzamidophenyl)-quinoline (IV), m.p. 124°, is obtained by benzoylation of the  $\text{NH}_2$ -derivative. Attempts to cyclise compounds (I)—(IV) have not been successful. Benzoylphenacylamine, m.p. 125—126°, prepared along with the  $\text{Bz}_2$  compound, m.p. 173—174°, from the corresponding amine, condenses with isatin in  $\text{EtOH} \cdot \text{KOH}$  to form 3-benzamido-2-phenylquinoline-4-carboxylic acid, m.p. 254—255°, which with  $\text{H}_3\text{PO}_4$  gives 3-amino-2-phenylquinoline [3-NHBz- (V), m.p. 179—180°, and 3-p-nitrobenzamido-derivatives, m.p. 223°]. Cyclisation of (V) with  $\text{P}_2\text{O}_5$  affords 2-phenyl-3 : 4 : 6 : 7-dibenzo-1 : 5-naphthyridine, m.p. 197—198° (monopicrate, m.p. 240—241°), whilst the corresponding Ac derivative yields an unidentified product, m.p. 199°. F. R. S.

**Synthesis of nitrogenous hetero-rings. XX. Synthesis of dibenzpyridocoline derivatives. III. Synthesis of 3' : 4' : 3'' : 4''-tetramethoxy-1 : 4 : 5 : 8-tetrahydro-2 : 3 : 6 : 7-dibenzpyridocoline [etc.].** S. Sugawara, K. Kakemi, and H. Kazumi (*Ber.*, 1940, 73, [B], 782—789; cf. A., 1939, II, 281).—Diveratryl ketone (prep. from *Pb homoveratrate* at 240—270°/vac.; not from alkaline-earth salts), m.p. 98—99° (oxime, m.p. 108—111°), with  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{HCO}_2\text{H}$  at 170—175° gives the N-CHO derivative, m.p. 129—130°, hydrolysed by hot 20%  $\text{HCl}$  to  $\beta\beta'$ -di-3 : 4-dimethoxyphenylisopropylamine (I), m.p. 88—89° (picrate, decomp. 147—149°; Bz derivative, m.p. 156°), and cyclised by  $\text{POCl}_3$  in xylene at 100° to 6 : 7-dimethoxy-3-veratryl-3 : 4-dihydroisoquinoline (II), an oil (perchlorate, m.p. 230—232°).  $\text{H}_2$  converts (II) in presence of  $\text{PtO}_2$  and a little  $\text{HCl}$  in  $\text{EtOH}$  into 6 : 7-dimethoxy-3-veratryl-1 : 2 : 3 : 4-tetrahydroisoquinoline hydrochloride, m.p. 206° [Bz derivative, m.p. 149—150°, of the base (III)], which with  $\text{CH}_2\text{O}$  in aq.  $\text{HCl}$  at 100° gives 3' : 4' : 3'' : 4''-tetramethoxy-1 : 4 : 5 : 8-tetrahydro-2 : 3 : 6 : 7-dibenzquinolizine [-pyridocoline] (IV), m.p. 283—284° (decomp.) [hydrochloride, +0.5 $\text{H}_2\text{O}$ , m.p. 272° (decomp.)]; methiodide, +4 $\text{H}_2\text{O}$ , brown at ~250°, decomp. 266°. Heating (III) in 90%  $\text{HCO}_2\text{H}$ , treating the product with  $\text{POCl}_3$  at room temp. and then 100° and finally with  $\text{KI}$  in dil.  $\text{HCl}$  gives 3' : 4' : 3'' : 4''-tetramethoxy-1 : 4 : 4a : 8-tetrahydro-2 : 3 : 6 : 7-dibenzpyridocolinium iodide, + $\text{H}_2\text{O}$ , m.p. 190—192° (decomp.), which absorbs 2 H (catalyst) to give (IV) and with I in  $\text{EtOH}$  gives the 1 : 4 : 5 : 8- $\text{H}_4$ -isomeride, m.p. 225—226° [also gives (IV) by hydrogenation (2 H)]. (I) gives (Schotten-Baumann) the N-homoveratryl derivative, m.p. 138—139°, converted ( $\text{PCl}_3$ -xylene) into 6 : 7-dimethoxy-1 : 3-diveratryl-3 : 4-di-, + $\text{H}_2\text{O}$ , m.p. 150° (hydrochloride, +1.5 $\text{H}_2\text{O}$ , decomp. 180°; picrate, +1.5 $\text{H}_2\text{O}$ , decomp. 196—197°), and thence -1 : 2 : 3 : 4-tetrahydroisoquinoline (V), m.p. 134—135° (hydrochloride, +0.5 $\text{H}_2\text{O}$ , decomp. 214—215°).  $\text{CH}_2\text{O}$ -aq.  $\text{HCl}$  at 100° converts (V) into a mixture, which by chromatography ( $\text{Al}_2\text{O}_3 \cdot \text{C}_6\text{H}_6$ ) gives 3' : 4' : 3'' : 4''-tetramethoxy-1-veratryl-1 : 4 : 5 : 8-tetrahydropyridocoline (VI), m.p. 172° (hydrochloride, decomp. 229—230°), and a mixture, m.p. 110—130°, possibly containing veratryltetrahydroisopalmitin. With, successively, 3 : 4 : 1-(OMe) $_2\text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{COCl} \cdot \text{NaOH}$ ,  $\text{POCl}_3$ -xylene, and  $\text{KI}$ , (III) gives 3' : 4' : 3'' : 4''-tetramethoxy-1-veratryl-4 : 4a : 5 : 8-tetrahydro-2 : 3 : 6 : 7-dibenzpyridocolinium iodide, +2 $\text{H}_2\text{O}$ , decomp. 183—184°, hydrogenated (2 H) in  $\text{EtOH}$  to (VI). R. S. C.

**Pyrazoles, pyridylpyrazoles, etc.**—See B., 1943, II, 302.

**Constitution of I-phenyl-d-fructosone.**—See A., 1943, II, 294.

**Effect of caffeine and other iminazole compounds on hæmatins and their derivatives.** J. Keilin (*Biochem. J.*, 1943, 37, 281—289).—When caffeine (I) is added to an alkaline solution of protohæm, the solution turns from reddish-brown to red and the two diffuse absorption bands are replaced by much stronger bands of shorter  $\lambda$ ; the solution is no longer opalescent, and no ppt. is formed on keeping. A similar effect is produced by (I) on meso-, deuterio-, and hæmato-hæm. The product so obtained is not a caffeine-hæmochromogen since the (I) combines with the porphyrin and not with the  $\text{Fe}^{++}$ . ~20 mols. of (I) per mol. of hæm or prophyrin are required for complete transformation. (I) also reacts with CO-protohæm (II), and the two absorption bands at 565 and 542  $\text{m}\mu$ . are shifted to 590 and 551  $\text{m}\mu$ ., respectively. Only 1 mol. of (I) per mol. of (II) is required to produce this change. (I) gives no reaction of this type with CO-hæms such as those derived from hæmato-, deuterio-, and meso-hæmatin. It is suggested that a CO-caffeine-hæmochromogen may be formed, or the (I) may react with the porphyrin. Only (I) and chlorocaffeine (III) out of a large no. of purines including theo-

bromine, theophylline, and 1 : 3 : 7-trimethyluric acid react in this way with hæm, (II), porphyrin, and metallo-porphyrins. The fact that (III) behaves like (I) shows that the H in position 8 can be replaced by Cl, but not by O. Thymine, cytosine, and uracil are without effect on various hæms or their porphyrins. Of all the glyoxaline compounds tested only pilocarpine, and to a smaller extent 1-methylglyoxaline, react like (I) with the porphyrin, but, in contrast to (I), they yield parahæmatin, hæmochromogen, and CO-hæmochromogen compounds with hæmatin, hæm, and CO-hæm respectively. Globin and certain serum-proteins react with porphyrin in the same manner as (I) does, whilst none of their constituent  $\text{NH}_2$ -acids including histidine gives the reaction, and it is suggested that either these proteins contain another, not yet isolated, constituent having the above properties, or that the glyoxaline ring of histidine, when it is part of a polypeptide chain, may have some of the properties of the glyoxaline rings of (I) and pilocarpine. The bearing of the results on the physico-chemical properties and pharmacology of (I), and on the mechanism of (I) diuresis, is discussed.

J. N. A.

**Chlorophyll-c.**—See A., 1943, III, 703.

**Benzthiazoles.**—See B., 1943, II, 302.

**Aldehydo-methylene derivatives of quinolines, benzoxazolines, and thiazolines.**—See B., 1943, II, 278.

**Quinolines ox- and thi-azolines.**—See B., 1943, II, 278.

**Thiazinocyanines. II. Cyanines containing the dihydro-1 : 3-thiazine nucleus.** (Miss) F. M. Hamer and R. J. Rathbone (*J.C.S.*, 1943, 243—249; cf. A., 1942, II, 182).—2-Thiotetrahydro-1 : 3-diazine with  $\text{Me}_2\text{SO}_4$  gives the 2-Me, b.p. 155—160°/50 mm., and with  $\text{Et}_2\text{SO}_4$  affords the 2-Et derivative, b.p. 145—150°/40 mm. The Me compound with MeI yields 2-methylthiodihydro-1 : 3-diazine methiodide (I), m.p. 132—133°, with considerable loss on crystallisation; the 2-Et ethiodide (II), m.p. 98°, is similarly obtained.  $\text{C}_5\text{H}_5\text{N}$  and (I) form 2-thio-3-methyltetrahydro-1 : 3-thiazine, m.p. 88°, and the 3-Et compound, similarly obtained, has m.p. 68°. 2-Methyldihydro-1 : 3-thiazine methiodide with  $\text{NPh}\cdot\text{CH}\cdot\text{NPh}$  gives 2- $\beta$ -anilino-1 : 3-thiazine methiodide, m.p. 165° (Ac derivative, m.p. 180—185°). 2-Methylbenzoxazole ethiodide,  $\text{NEt}_3$ , and (II) in EtOH afford [2-(3-ethyl-dihydro-1 : 3-thiazine)][2-(3-ethylbenzoxazole)]-, m.p. 260° (decomp.), and [2-(3-methyldihydro-1 : 3-thiazine)][2-(3-ethyl-6 : 7-benzbenzoxazole)]-methincyanine iodide, m.p. 264° (decomp.) is prepared from (I),  $\text{NEt}_3$ , and 2-methyl-6 : 7-benzbenzoxazole ethiodide. [2-(3-Methyldihydro-1 : 3-thiazine)][2-(3-methylbenzthiazole)]-methincyanine iodide, m.p. 283° (decomp.), is obtained from (I), 2-methylbenzthiazole methiodide, and  $\text{K}_2\text{CO}_3$ , whilst the corresponding Et derivative, m.p. 265° (decomp.) (lit. decomp. 238°), is prepared from (II) and the ethiodide. Similar preps. are made from (I) or (II) with the appropriate benzthiazole derivative: [2-(3-methyldihydro-1 : 3-thiazine)][2-(3-methyl-4 : 5-, m.p. 226° (decomp.)) [Et compound, m.p. 238° (decomp.)], and -6 : 7-benzbenzthiazole)]-methincyanine iodide, m.p. 267° (decomp.) [Et compound, m.p. 254° (decomp.)]; [2-(3-ethyl-dihydro-1 : 3-thiazine)][2-(5-chloro-3-ethylbenzthiazole)]-, m.p. 251° (decomp.), [2-(3-methyldihydro-1 : 3-thiazine)][2-(6-chloro-, m.p. 283° (decomp.)), -6-acetamido-, m.p. 279° (decomp.)], and -3(ethylbenzthiazole)]-methincyanine iodide, decomp. 249°; [2-(3-ethyl-dihydro-1 : 3-thiazine)][2-(3-ethylbenzthiazole)]-methincyanine iodide, m.p. 264° (decomp.), and the corresponding Me derivative, m.p. 271° (decomp.); [2-(3-methyldihydro-1 : 3-thiazine)][2-(1-methylquinoline)]-, m.p. 225° (decomp.), [2-(1-ethylquinoline)]-, m.p. 189° (decomp.) [Et derivative, m.p. 169° (decomp.)], [4-(1-methylquinoline)]-, m.p. 164—165° (decomp.), and [4-(1-ethylquinoline)]-methincyanine iodide, m.p. 202° (decomp.) [Et derivative, m.p. 191° (decomp.)]; bis-2-(3-methyldihydro-1 : 3-thiazine)trimethincyanine iodide, m.p. 188° (decomp.), and the Et derivative, m.p. 243° (decomp.); [2-(3-methyldihydro-1 : 3-thiazine)][2-(3-ethylbenzoxazole)]-, m.p. 270° (decomp.), and -3(ethylbenzthiazole)]-trimethincyanine iodide, m.p. 275° (decomp.); 5 : 2'-(3'-ethyltetrahydro-1' : 3'-thiazyl)-3-ethylrhodanine, m.p. 102°; 5 : 2'-(3'-methyltetrahydro-1' : 3'-thiazyl)ethylidene-3-rhodanine, m.p. 195° (decomp.); and 5 : 2'-(3'-methyltetrahydrothiazolyl)ethylidene-3-ethylrhodanine, m.p. 219° (decomp.). Absorption max. of the various dyes have been compared. Replacement of the thiazoline by the dihydro-1 : 3-thiazine nucleus produces a bathochromic shift.

F. R. S.

## VII.—ALKALOIDS.

**Alkaloids of *Thermopsis rhombifolia* (Nutt.), Richards.** R. H. F. Manske and L. Marion (*Canad. J. Res.*, 1943, 21, B, 144—148; cf. A., 1943, III, 294).—*T. rhombifolia* (excluding roots) contains *N*-methylcystisine (0.107), thermopsine (0.048), 3-methoxypyridine, rhombifoline (0.022),  $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_2$  (?) (perchlorate, m.p. 242°; picrate, m.p. 207°), cytisine (0.009), rhombinine (0.004%),  $\text{C}_{16}\text{H}_{22}\text{O}_2\text{N}_2$  (?) [perchlorate, m.p. 313° (bath preheated to 305°); picrate, m.p. 253°], and neutral compounds A,  $\text{C}_{19}\text{H}_{20}\text{O}_{10}$ , m.p. 218—220°, and B,  $\text{C}_{22}\text{H}_{14}\text{O}_6$ , m.p. 257°. All m.p. are corr.

A. Li.

**Alkaloids of papaveraceous plants. XXXVIII. *Bocconia arborea*, Wats.** R. H. F. Manske (*Canad. J. Res.*, 1943, 21, B, 140—143).—*B. arborea* (excluding roots) contains chelerythrine (0.86), protopine (0.04%), allocryptopine, alkaloid P61,  $\text{C}_{21}\text{H}_{19}\text{O}_5\text{N}$  (? 2 OMe and 1 NMe groups), m.p. 210°, and neutral compounds A,  $\text{C}_{20}\text{H}_{17}\text{O}_4\text{N}$ , m.p. 302°, B,  $\text{C}_{20}\text{H}_{15}\text{O}_4\text{N}$ , m.p. 191°, and C,  $\text{C}_{31}\text{H}_{33}\text{O}_5\text{N}$ , m.p. 332° (shrinks at 327°). Phenolic alkaloids are absent. All m.p. are corr.

A. Li.

**Synthesis of compounds related to lysergic acid.** H. W. Murphy and G. L. Jenkins (*J. Amer. Pharm. Assoc.*, 1943, 32, 83—89).—Aq.  $p\text{-NH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}\cdot\text{HCl}$  (I) with  $\text{COMe}_2$  gives acetone- $p$ -carboxyphenylhydrazine, m.p. 230° (decomp.), which, when heated with anhyd.  $\text{ZnCl}_2$  to 175—185°, yields 2-methylindole and not the expected 2-methylindole-5-carboxylic acid. Similarly, *n*-butaldehyde- $p$ -carboxyphenylhydrazine, m.p. 170°, failed to yield the expected indole derivative. Na 1 : 2 : 3 : 4-tetrahydrocarbazole-6-carboxylic acid (1 mol.) [from cyclohexanone- $p$ -carboxyphenylhydrazine (Collar and Plant, A., 1926, 735)] with dry  $\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{NHEt}_2\text{Cl}$  (II) (1 mol.) (Gough and King, A., 1928, 1231) at 150° for 1½ hr., liberation of base by aq.  $\text{NH}_3$ , and treatment with  $\text{Et}_2\text{O}\cdot\text{HCl}$  affords  $\beta$ -diethylaminoethyl-1 : 2 : 3 : 4-tetrahydrocarbazole-6-carboxylate hydrochloride, m.p. 241—242°. cyclohexanone- $m$ -carboxyphenylhydrazine yields on cyclisation with 20%  $\text{H}_2\text{SO}_4$  two acids, m.p. 286° and 212°, probably 1 : 2 : 3 : 4-tetrahydrocarbazole-5- and -7-carboxylic acid, but neither gave the corresponding acid chloride with  $\text{SOCl}_2$  or  $\text{SOCl}_2\cdot\text{C}_6\text{H}_5\text{N}$ .  $o\text{-NH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  (from anthranilic acid) is freed from  $o$ -diazobenzimide by reduction with  $\text{Zn}\cdot\text{AcOH}$ , addition of  $\text{HCl}$ , and removal of the imide by filtration; with cyclohexanone, the acid (warm, aq. hydrochloride) gives cyclohexanone- $o$ -carboxyphenylhydrazine, m.p. 162°, cyclised by 20%  $\text{H}_2\text{SO}_4$  to 1 : 2 : 3 : 4-tetrahydrocarbazole-8-carboxylic acid, m.p. 203° (Et ester, m.p. 76°), the Na salt of which with dry (II) at 150° for 2 hr. and treatment as above gives  $\beta$ -diethylaminoethyl-1 : 2 : 3 : 4-tetrahydrocarbazole-8-carboxylate hydrochloride, m.p. 208°. In an attempt to prepare 4-chloro-1 : 2 : 3 : 4-tetrahydrocarbazole-6-carboxylic acid, 2-chlorocyclohexanone is treated with excess of  $\text{NHEt}_2$  in presence of NaI at room temp., giving (2-keto-1-cyclohexyl)diethylamine [2-diethylaminocyclohexanone], b.p. 188°/742 mm. (hydrochloride, m.p. 226—228°). Camphor in EtOH, refluxed with (I) and NaOAc for 2 hr., gives camphor- $p$ -carboxyphenylhydrazine, m.p. 251°; attempts to cyclise this to 1-methyl-1 : 4-(dimethylmethylene)-1 : 2 : 3 : 4-tetrahydrocarbazole-6-carboxylic acid failed, as did attempts to prepare the corresponding -8-carboxylic acid from camphor- $o$ -carboxyphenylhydrazine, m.p. 224—226° (decomp.). Et cyclohexan-2-one-1-carboxylate with diazotised  $p$ -phenetidine gives 1-Et 2-ketopimelate  $p$ -ethoxyphenylhydrazine, m.p. 114°, cyclised by 10%  $\text{H}_2\text{SO}_4$  in EtOH to  $\text{Et}_2\gamma$ -(2-carboxy-5-ethoxy-3-indolyl)butyrate, m.p. 93°; the free acid, m.p. 206°, is decarboxylated by heating with a small amount of powdered glass to 220—230° to  $\gamma$ -(5-ethoxy-3-indolyl)butyric acid, m.p. 133° [Et (III), m.p. 69°, and Me ester (IV), m.p. 84°] (III) is reduced (EtOH-Na) to  $\delta$ -5-ethoxy-3-indolyl-butyl alcohol, b.p. 215°/2 mm. (phenylurethane, m.p. 117—118°). (IV) with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}\cdot\text{EtOH}$  at 130—145° yields  $\gamma$ -(5-ethoxy-3-indolyl)-butyrhydrazide, m.p. 157°, which with aq.  $\text{HNO}_2$  at 0° gives the corresponding azide; this added in small amounts to  $\text{H}_2\text{O}$  at 100° fails to yield  $\text{NN}'$ -bis-(5-ethoxy-3-indolyl)propylcarbamide, but the waste liquor affords  $\gamma$ -(5-ethoxy-3-indolyl)propylammonium chloride, m.p. 205°.

F. O. H.

**Strychnine alkaloids. CX. Strychnone and  $\psi$ -strychnone as by-products of the preparation of  $\psi$ -strychnine. Further experiments in the series. CXI. Transformations of dihydro- $\psi$ -strychnine.** H. Leuchs and F. Räck (*Ber.*, 1940, 73, [B], 731—739, 811—817).—CX. The neutral by-products (10—15%) obtained during oxidation of strychnine (I) in  $\text{CHCl}_3$  by Fehling's solution (A., 1937, II, 435) contain strychnone (II) (3—4.5%),  $\text{C}_{21}\text{H}_{20}\text{O}_3\text{N}_2$ , sinters 240°, m.p. ~268° (decomp.; vac.),  $[\alpha] -667^\circ/d$  in  $\text{CHCl}_3$ , and  $\psi$ -strychnone (III) (~0.5%),  $\text{C}_{21}\text{H}_{20}\text{O}_4\text{N}_2$ , m.p. 315—317° (decomp.; vac.),  $[\alpha] +33.3^\circ/d$  in  $\text{CHCl}_3$ . In (II) the  $\text{CH}_2$  next to N-b has been oxidised to CO, so that (II) is "diamidostrychnine" and its neutral properties are accounted for.  $\text{H}_2\text{-PtO}_2$  converts (II) in 50% AcOH into a  $\text{H}_2$ -derivative, m.p. 165—175° (vac.),  $[\alpha] -365^\circ/d$  in  $\text{CHCl}_3$ . 12N-HCl at room temp. hydrolyses (II) to the  $\text{NH}_2$ -acid, "strychnone hydrate" (IV), sinters 200°, m.p. 220—225° (vac.), and an amorphous, blue product,  $\text{C}_{42}\text{H}_{38}\text{O}_6\text{N}_2\cdot\text{HCl}$ . (IV) is sol. in  $\text{NH}_3$  or  $\text{HCl}$ ; its hydrochloride is readily hydrolysed.  $\text{Ac}_2\text{O}$  at 100° reconverts (IV) into (II).  $\text{H}_2\text{-PtO}_2$  converts (III) in 50% AcOH into its  $\text{H}_2$ -derivative, sinters 290°, m.p. ~330° (decomp.; vac.),  $[\alpha] +116^\circ/d$  in AcOH, previously obtained as an impurity in dihydro- $\psi$ -strychnine. Adding  $\text{SO}_2$  to strychnine oxide in warm aq.  $\text{HCl}$  gives (I) and an inner salt,  $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2\cdot\text{SO}_3$ , m.p. 270—275° (decomp.; vac.), containing a semipolar N-S linking.  $\psi$ -Strychnine reacts with aq.  $\text{SO}_2$  only in presence of pptd.  $\text{MnO}_2$ ; warming this mixture gives C-sulphonic acids, (a) decomp. 280—305°,  $[\alpha] -150^\circ/d$  in 0.1N-NaOH, and (b) +5 $\text{H}_2\text{O}$ ,  $[\alpha]$  (anhyd.) -189°/d in 0.1N-NaOH. At 100—125°/vac., (b) becomes orange and loses >5  $\text{H}_2\text{O}$ , presumably forming an anhydro-salt or lactone. Zn dust in boiling 50% AcOH converts (a) into strychninesulphonic acid-I,  $[\alpha] -230^\circ$  in 0.1N-NaOH. *N*-Methyl-sec- $\psi$ -strychnine (V), with  $\text{SO}_2\cdot\text{MnO}_2$  also gives a mixture;

a sulphonic acid,  $[\alpha] -128.0^\circ/d$ , and a mixture,  $[\alpha] -31.8^\circ/d$  in 0.1N-NaOH, are isolated. Although a ketone, (V) gives no oxime and in aq. HBr (1 mol.) gives only a  $Br_1$ -compound (50%) [perchlorate (VI); Br is attached to a  $C_6H_5$  nucleus]. Only amorphous material is obtained from (V) by  $KMnO_4$ - $COMe_2$ . The methoperochlorate (VII) of (V) and Br (4 atoms) in  $H_2O$  give similarly only a perbromide, whence  $SO_2$  yields the  $Br_1$ -derivative methoperochlorate, sinters  $250^\circ$ , decomp.  $265-270^\circ$ . With NaOMe, (VII) gives the O-Me ether (VIII),  $C_{23}H_{30}O_3N_2$  (contains  $C:O-Me$ ), which with aq.  $NH_2OH$ , HCl at  $100^\circ$  and then  $HClO_4$ , or a trace of hot  $HClO_4$ , yields the methoperochlorate,  $C_{22}H_{24}O_3N_2 \cdot MeClO_4$ , m.p.  $290-295^\circ$  (decomp.). With  $Br-CHCl_3$  at  $0^\circ$  and then aq.  $HClO_4$ , (VIII) gives a perbromide and thence a  $Br_2$ -derivative methoperochlorate,  $C_{22}H_{22}O_3N_2 \cdot Br_2 \cdot MeClO_4$ , decomp.  $260-330^\circ$ . Reduction of the methiodide of (VIII) by Na-Hg in  $H_2O$  gives an amorphous mixture, whence MeI yields a small amount of a salt,  $C_{24}H_{30}O_3N_2 \cdot MeI$ , m.p.  $275-278^\circ$  (decomp.); Na-Hg reduces (VIII) in MeOH to a product, m.p.  $170-172^\circ$  (vac.). Oxidation of (VIII) by  $KMnO_4$ - $COMe_2$  gives no identifiable products; that of the ether,  $C_{24}H_{32}O_3N_2$  (IX), results only in hydrolysis to the base,  $C_{23}H_{30}O_3N_2$  (perchlorate). The base,  $C_{24}H_{34}O_3N_2$ , m.p.  $128^\circ$  (A., 1938, II, 208), with CNBr in  $C_6H_6$  gives the quaternary salt (derived perchlorate, m.p.  $\sim 280^\circ$ ) and cyanoamide,  $C_{24}H_{31}O_3N_2$ , m.p.  $110^\circ$  (decomp.); (IX) gives similarly a quaternary salt [derived methoperochlorate,  $C_{23}H_{30}O_3N_2 \cdot MeClO_4$ , m.p.  $295-300^\circ$  (decomp.)] and cyanoamide,  $C_{24}H_{29}O_3N_3$ , sinters  $155^\circ$ , m.p.  $165-166^\circ$ . The base,  $C_{23}H_{28}O_3N_2$ , obtained by reducing the methiodide of (V) by Na-Hg, with  $KMnO_4$  in  $COMe_2$  at  $0^\circ$  gives 10% of a neutral substance,  $C_{23}H_{28}O_4N_2$ , m.p.  $295^\circ$  (vac.), containing  $CO-N(b)$ .

CXI.  $H_2$ -PtO<sub>2</sub> converts  $\psi$ -strychnine in HCl- $H_2O$ -AcOH partly into dihydro- $\psi$ -strychnine (X),  $C_{21}H_{24}O_3N_2$ , m.p.  $240-243^\circ$  (vac.),  $[\alpha] +38.7^\circ/d$  (lit.  $+34.5^\circ$ ) in  $CHCl_3$ , which is purified as hydrochloride or hydrobromide and gives the Me ether (XI), m.p.  $\sim 209^\circ$  (vac.). With  $Cl_2-CCl_4$ , (X) in HCl gives a  $Cl_1$ -derivative, sinters  $270^\circ$ , m.p.  $280-282^\circ$  (decomp.; vac.),  $[\alpha] -59.7^\circ/d$  in  $CHCl_3$ , best isolated by way of the Me ether, m.p.  $212-215^\circ$  (vac.),  $[\alpha] +51^\circ/d$  in  $CHCl_3$ . With aq. Br-HBr, (X) gives the  $Br_1$ -derivative, m.p.  $240-244^\circ$  (decomp.; vac.),  $[\alpha] -61^\circ$  in  $CHCl_3$  [Me ether, m.p.  $205-207^\circ$  (vac.)]. With PhCHO and NaOMe-MeOH, (XI) gives a little benzylidene-, m.p.  $209-215^\circ$ ,  $[\alpha] -108^\circ/d$  in  $CHCl_3$  (positive Otto reaction) (much  $\psi$ -derivative is formed), and thence (Na-Hg in HCl-MeOH- $H_2O$ ) benzyl- $\psi$ -dihydrostrychnine, m.p.  $208-212^\circ$  (vac.), decomp.  $220^\circ$  [m.p.  $235-238^\circ$  (decomp.; vac.)] (hydrochloride), which is also obtained by catalytic hydrogenation of benzylidene- or benzyl- $\psi$ -strychnine, m.p.  $125-135^\circ$  (vac.), decomp.  $145^\circ$ . Boiling NaOMe-MeOH converts (X) into isodihydro- $\psi$ -strychnine Me ether (XII), sinters at  $325^\circ$ , m.p.  $\sim 345^\circ$  (decomp.; block),  $[\alpha] +116^\circ/d$  in  $CHCl_3$ , which yields isodihydro- $\psi$ -strychnine, m.p.  $332-334^\circ$  (decomp.; vac.) [ $CHPh$  derivative, m.p.  $190-192^\circ$  (decomp.) (negative Otto reaction)]; this absorbs 6 H (PtO<sub>2</sub>; HCl-AcOH- $H_2O$ ), yielding 13.4% of a base,  $C_{21}H_{28}O_2N_2$ , m.p.  $226-228^\circ$ ,  $[\alpha] -42^\circ$  in  $CHCl_3$  (perchlorate, sinters  $\sim 141^\circ$ ), previously (A., 1934, 312) obtained from isodihydrostrychnine and in which  $N(a) \cdot CO \cdot CH_2 \cdot CH \cdot O \cdot CH_2$  has been converted into  $N \cdot CO \cdot CH:CH + OH \cdot CH_2$ . In  $Ac_2O$  (blue solution) or  $Ac_2O-C_5H_5N$  at  $100^\circ$ , (XII) gives the ON- $Ac_2$  derivative, m.p.  $248-250^\circ$  (decomp.; vac.). In  $Ac_2O$  at  $100^\circ$ , (X) or (XI) gives a salt,  $C_{23}H_{27}O_4N_2ClO_4$ , m.p.  $\sim 280-285^\circ$  (decomp. from  $270^\circ$ ; block), and  $\sim 10\%$  of the N- $Ac$  derivative, m.p.  $267-269^\circ$  (decomp.; vac.) (the main product formed by  $Ac_2O-C_5H_5N$ ); this salt absorbs 6 H (PtO<sub>2</sub>- $H_2O$ ) to give a product, m.p.  $\sim 290^\circ$  (decomp.), of uncertain composition.  $[\alpha]$  are  $[\alpha]_D^{20}$ . R. S. C.

Veratrine alkaloids. XIX. Protoveratrine and its alkamine, protoverine. W. A. Jacobs and L. C. Craig (J. Biol. Chem., 1943, 149, 271-279; cf. A., 1942, II, 240).—Protoveratrine (I),  $C_{39}H_{61}O_{13}N$ , decomp.  $275^\circ$  (depends on rate of heating) after darkening and sintering, and warm aq. NaOH-MeOH, followed by  $CHCl_3$  extraction and saturation with  $CO_2$  [limits formation of (III)], give, after decomp. of the  $CHCl_3$  compound, protoverine (II),  $C_{27}H_{43}O_9N$ , anhyd. (dried at  $120^\circ/2$  mm.) or  $+H_2O$ , slowly softens and melts at  $210-216^\circ$ , or  $+2MeOH$ , softens to a resin at  $195-200^\circ$ ,  $[\alpha]_D^{25} -12^\circ$  in  $C_5H_5N$ . A little isoprotoverine (III), decomp.  $264^\circ$  after sintering and darkening,  $[\alpha]_D^{25} -42^\circ$  in  $C_5H_5N$ , is also isolated, and it can be obtained by isomerisation of (II) with aq. MeOH-NaOH at  $50^\circ$ . (II) and  $COMe_2$ -HCl-MeOH yield acetonylprotoverine,  $C_{30}H_{47}O_9N$ , sinters and colours at  $>235^\circ$ , and gradually melts to a dark mass at  $253-256^\circ$  [hydrochloride, m.p.  $278-281^\circ$  (decomp.), after sintering]; (I) does not give a similar derivative. (II) and Na-BuOH (but not  $H_2$ -PtO<sub>2</sub>) afford a  $H_2$ -compound, decomp.  $>300^\circ$ , increasing decomp. at  $330-335^\circ$ ,  $[\alpha]_D^{25} -54^\circ$  in  $C_5H_5N$ . (III) and  $H_2$ -MeOH-PtO<sub>2</sub> yield a  $H_2$ -derivative, slow decomp. at  $315-320^\circ$  after softening and discoloration,  $[\alpha]_D^{25} -49^\circ$  in  $C_5H_5N$ . (II) behaves as a *tert.* base, and contains a double linking and probably 9 OH groups, and is a hexacyclic *tert.* sterol base. Structures of (I) and (II) are discussed, and the relation between veratrine and potato alkaloids is noted (cf. Prelog *et al.*, A., 1943, II, 106). A. T. P.

Lunamaridine,  $C_{16}H_{15}O_2N$ , m.p.  $209-210^\circ$ , from bark of *Lunasia amara*.—See A., 1943, III, 675.

L 3 (A., II.)

## VIII.—ORGANO-METALLIC COMPOUNDS.

Mercurated aryl alkyl ketones.—See B., 1943, III, 225.

## IX.—PROTEINS.

Polarographic researches on proteins. I. Polarography as a research method. C. Tropp. II. Application to changes of state of fibrinogen. L. Jühling, C. Tropp, and E. Wohlisch. III. Albumin, globulin, fibrinogen, plasma, and serum. C. Tropp, L. Jühling, and F. Geiger (Z. physiol. Chem., 1939, 262, 199-209, 210-224, 225-242).—I. An exposition of the method and its application to proteins.

II. Pure fibrinogen (I) behaves polarographically like other S-containing proteins, giving the typical double step curve. Heat-denaturation of (I) in 10%  $CO(NH_2)_2$  solution causes elevation of both protein steps. When treated with thrombin in 10%  $CO(NH_2)_2$  the corresponding elevation of both steps is only seen after dilution of the  $CO(NH_2)_2$  content to 3%. Trypsin elevates both protein steps at room temp. and at  $40^\circ$ . When the action of the enzyme is prolonged, the first step disappears and the second is flattened. The first step is correlated with the acid-amide linking. The elevation of the second step marks the increase in cystine materials due to enzyme action. The flattening of the second step denotes that under the influence of continued alkaline enzymic hydrolysis the liberated cystine escapes detection owing to oxidation.

III. Albumin and globulin (II), like (I), show a definite elevation of both protein steps on heat-denaturation. The max. protein concn. permitting polarographic analysis is for (II) 3.2%, for (I) 0.48%, for other proteins intermediate concns. The polarographic dilution curves are shown as plane diagrams which differ for each protein. All show a "cross-over effect" due to the lowering of the second below the first step. At high dilutions all the protein systems show similar behaviour. The plasma and serum diagrams are interpreted as interference diagrams of the corresponding basal proteins. The proteins examined can all be differentiated polarographically. J. H. B.

Fractionation of protein mixtures by electrophoresis. H. Gutfreund (Biochem. J., 1943, 37, 186-189).—Proteins are separated by electro dialysis in a buffer at the isoelectric point of the one to be purified. The others collect at the top or bottom of the cell, and are separated by carefully removing suitable portions of the cell contents, leaving the desired protein electrically homogeneous. R. L. E.

Iron proteins of spleen. Structure of ferritin. R. Kuhn, N. A. Sørensen, and L. Birkofer (Ber., 1940, 73, [B], 823-837).—Ferritin (I) is obtained by Laufberger's method (A., 1938, III, 208) from the spleen of horses, dogs, cats, or jackals, but not from that of guinea-pigs, rabbits, or a whale, although the spleen of the latter group was rich in Fe. Spleen containing (I) is stable at  $80^\circ$ ; others coagulate. (I) is dimorphic and has  $[\alpha]_D^{21} \pm 30^\circ$  in  $H_2O$ . All the Fe is  $Fe^{+++}$ , being liberated as  $Fe^{+++}$  by dil. HCl but unaffected by 2:2'-dipyridyl. Reduction to  $Fe^{++}$  is impossible without removal of Fe from the mol. (I) has no catalase, peroxidase, tyrosinase, aldehyde-dehydrase or -mutase action, confirming the view that biological catalysts function only when a change of valency is possible. The Fe content of (I) can usually be raised to  $\sim 21\%$  (cf. *loc. cit.*), but occasionally to 24%. Dialysis against N-HCl removes the Fe and all the P. The S is entirely accounted for as cysteine (II) and methionine (III). Hydrolysis by boiling 6N- $H_2SO_4$  gives  $Fe_2(SO_4)_3$ ,  $H_3PO_4$ , guanine, adenine, thymine, cytosine, a reducing sugar (IV) (? deoxyribose; gives no pentose reaction), and  $NH_2$ -acids. Determination of the N content of the purines, the reducing power of (IV), and the  $H_3PO_4$  indicate that these ingredients are totally accounted for as the thymonucleic acid of Levene *et al.* (cf. A., 1908, i, 587). (I) containing 21.1% of Fe contains also 54.5% of protein and 12.1% of nucleic acid; the residual 33.4% necessitates the Fe being present as  $FeO_2H$  (theory 33.6%) and excludes its presence as  $Fe(OH)_3$ . The absorption spectrum of (I) (steady rise in  $\epsilon$  from 0 at 600  $m\mu$ . to  $\sim 2300$  at  $\sim 380$   $m\mu$ .; no max.) resembles that of  $Fe(NO_3)_3$  at pH 6.6 (acetate buffer), confirming the presence of  $Fe^{+++}$ . Quant. measurement of the pptn. by  $(NH_4)_2SO_4$  confirms the homogeneity of (I). Determination of various  $NH_2$ -acids shows that no one  $NH_2$ -acid can be attached to all the Fe; the following mol. composition is indicated by these analyses: arginine 72, histidine 2, lysine 24, glycine 18, phenylalanine 6 or 8, tyrosine 48, tryptophan ? 6, (II) 12, (III) 12, S 24, P 48, Fe 470 (?  $2 \times 288 = 576$ ). It is thus probable that for (I) containing 24% of Fe each peptide linking corresponds to 1 Fe atom. R. S. C.

## X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lichen substances. XCV. Zeorin group. II. Y. Asahina and I. Yosioka (Ber., 1940, 73, [B], 742-747; cf. A., 1938, II, 289).—Yields of atranorin and zeorin (I), respectively, are from *Anaptychia*

*speciosa*, Mass., 4.1 and 1.0, *A. hypoleuca* (Muelenb.), Wain., 3.4 and 1.4, and *A. heterochroa*, Wain., 1.2 and 0.45% [contains also a (? hydroxyanthraquinone) dye, ? blastenin, m.p. 278°]. In  $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$  at 75°, (I) gives the acetate, m.p. 225—227° (*loc. cit.*, m.p. 178°), which gives no colour with  $\text{C}(\text{NO}_2)_4$ . Boiling  $\text{AcOH}$  dehydrates (I) to anhydrozeorin acetate (II), m.p. 211—215° (*loc. cit.*, 158°),  $[\alpha]_D^{20} + 94.52^\circ$  in  $\text{CHCl}_3$ , and mixed isomerides (III), m.p. 65—75°. Crude (II) and (III) are hydrolysed by boiling 20%  $\text{KOH}-\text{MeOH}$  to pure (m.p. 211—214°) and impure anhydrozeorin,  $\text{C}_{30}\text{H}_{50}\text{O}$ , respectively.  $\text{HCl}-\text{EtOH}$  dehydrates (I) to zeorinin (IV),  $\text{C}_{30}\text{H}_{50}\text{O}$ , m.p. 181—183°,  $[\alpha]_D^{20} + 50.0^\circ$  in  $\text{CHCl}_3$  [yellow in  $\text{C}(\text{NO}_2)_4$ ; acetate (V), m.p. 197—200°; reddish-violet Liebermann reaction].  $\text{Na}_2\text{Cr}_2\text{O}_7$  oxidises (IV) in  $\text{AcOH}$  at  $>60^\circ$  to zeorinone,  $\text{C}_{30}\text{H}_{48}\text{O}$  (CO in place of  $\text{CH}_2$ ), m.p. 184° (no acetate or oxime). With  $\text{CrO}_3-\text{AcOH}$  at 60—65°, (V) gives a saturated  $[\text{C}(\text{NO}_2)_4]$  acetate,  $\text{C}_{32}\text{H}_{52}\text{O}_4$ , m.p. 230—236° [oxime, m.p. 293° (decomp.)], containing CO in place of  $\text{CH}_2$  and  $\text{CH}\cdot\text{C}-\text{OH}$  in place of  $\text{C}\cdot\text{C}$ .  $\text{BzO}_2\text{H}-\text{CHCl}_3$  or 30% aq.  $\text{H}_2\text{O}_2$  in  $\text{AcOH}$  converts (IV) into zeorinin oxide (VI), m.p. 286—289° (289°),  $[\alpha]_D^{20} + 62.5^\circ$  in  $\text{CHCl}_3$  [acetate, m.p. 255—257°, also obtained from (V) and hydrolysed by  $\text{KOH}-\text{MeOH}$  to (VI)], which with conc.  $\text{HCl}-\text{EtOH}$  at 100° gives isodehydrozeorinin (VII), m.p. 183—185.5° [reddish-violet Liebermann reaction; orange red in  $\text{C}(\text{NO}_2)_4$ ; acetate, m.p. 223—227°]. (VII) contains 2 C:C and, when hydrogenated (Pt-black;  $\text{AcOH}$ ), slowly absorbs 2 H to regenerate (IV) having the difficultly reducible C:C.  $\text{H}_2-\text{Pd}$ -black reduces (IV) to deoxyzeorin (VIII),  $\text{C}_{30}\text{H}_{52}\text{O}$ , m.p. 166—167°,  $[\alpha]_D^{20} + 48.62^\circ$  in  $\text{CHCl}_3$  (red Liebermann reaction; no colour in  $\text{C}(\text{NO}_2)_4$ ; acetate, m.p. 182—183°), oxidised by  $\text{CrO}_3-\text{AcOH}$  at room temp. to deoxyzeorinone,  $\text{C}_{30}\text{H}_{50}\text{O}$ , m.p. 164—165°,  $[\alpha]_D^{20} + 16.87^\circ$ , unchanged by  $\text{SeO}_2$  at 100° and reduced by  $\text{Na}-\text{EtOH}$  to (VIII). R. S. C.

**Mould tissue. XVI. Isolation of fungus cerebrin from the mycelium of *Aspergillus sydowi*.** N. Bohonos and W. H. Peterson (*J. Biol. Chem.*, 1943, **149**, 295—300; cf. A., 1938, III, 151).—A cryst. lipin (I),  $\text{C}_{46}\text{H}_{93}\text{O}_5\text{N}$ , m.p. 142.5—143°,  $[\alpha]_D^{25} + 11.9^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , obtained from *A. sydowi*, is probably identical with fungus cerebrin (Reindel *et al.*, *Annalen*, 1940, **544**, 116). (I), obtained by  $\text{Et}_2\text{O}$  extraction of the insol. residue after autolysis and alkali extraction of the mycelium, is purified through the tetra-acetate,  $\text{C}_{54}\text{H}_{101}\text{O}_9\text{N}$ , m.p. 67—67.5°,  $[\alpha]_D^{25} + 20.6^\circ$  in  $\text{CHCl}_3$ . (I) appears to be bound in mould tissue, as it is not obtained from unautolysed mycelium. It is degraded at 235°,  $\text{H}_2\text{O}$  is lost, and a product, m.p. 74—75° (softens at 71°), is obtained. (I) and  $\text{Pb}(\text{OAc})_4-\text{CHCl}_3-\text{AcOH}$  at 40—50° yield (a) a ketone,  $\text{C}_{18}\text{H}_{32}\text{O}$  (dinitrophenylhydrazone, m.p. 94—95°), and (b) a product hydrolysed by boiling  $\text{HCl}-\text{MeOH}$  to (probably) a compound,  $\text{C}_4\text{H}_8\text{O}_3$  (2:4-dinitrophenylhydrazone, decomp. 270—280°), and (mainly) the Me ester, m.p. 68—71°, of a OH-acid; the free acid (II),  $\text{C}_{26}\text{H}_{52}\text{O}_3$ , m.p. 102.5—104.5° ( $\text{NH}_4$  salt; chloral derivative, m.p. 65—66°), is obtained by boiling  $\text{KOH}-\text{EtOH}$ . (II) and  $\text{Pb}(\text{OAc})_4-\text{AcOH}$  give (probably) an aldehyde (semicarbazone, m.p. 113.5—114°). Data confirm the structure suggested for fungus cerebrin by Reindel *et al.*, who also prepared similar derivatives. A. T. P.

**Caneine**,  $\text{C}_{15}\text{H}_{24}\text{O}_3\text{N}_2$ , m.p. 188—189° (picrate, m.p. 120—121°), and **kitagine**,  $\text{C}_7\text{H}_7\text{O}_3\text{N}$ , m.p. 240—242°, from jack beans.—See A., 1943, III, 702.

**Lignin. XL. Enzymic degradation of polymeric carbohydrates. VII. Fractionation of linden wood and enzymic degradation of the fractions.** T. Ploetz (*Ber.*, 1940, **73**, [B], 790—794).—When linden wood (*Tilea tomentosa*) is digested for 14 days with  $(\text{CH}_2\cdot\text{NH}_2)_2-\text{CuO}$ , ~34% of a residue (A) is obtained. Acid ppts. ~42% from the solution; ~24% remains sol. The components of lower OMe content are preferentially dissolved. A fraction containing 75% of pentosan had 3.28% of OMe, indicating that the OMe of the sugars occurs mainly in the pentosans. (A) is rapidly attacked by snake venom (cf. *loc. cit.*); up to 50% degradation the loss in wt. is accounted for by the sugar in solution; thereafter discrepancies occur. 58.5% degradation is finally achieved; the insol. material (B) is then a 1:1 lignin-sugar complex, containing only a little pentose. Treatment of (B) with  $(\text{CH}_2\cdot\text{NH}_2)_2-\text{CuO}$  leaves 8.8% of residue, containing 78.9% of lignin; acid ppts. from the solution a small amount of material which is degraded enzymically to the 1:1 complex, which now contains no pentose. Treating the solution from (B) with acid gives a product, which suffers 62.1% of enzymic degradation, the insol. portion (C) then containing 39% of lignin. Repetition on (C) of the two degradative procedures gives an insol. material containing 53.8% of lignin, i.e., the 1:1 complex. R. S. C.

**Reaction of sulphanilamide [with lignin].**—See A., 1943, II, 298.

**Lignin esters.**—See B., 1943, II, 281.

## XI.—ANALYSIS.

**New technique for ultimate micro-analysis of organic compounds.** R. Belcher and C. E. Spooner (*J. C.S.*, 1943, 313—316).—A technique is described for the micro-determination of C, H, S, and halogens in

org. compounds, by combustion at 800° in a rapid stream of  $\text{O}_2$  (50 ml. per min.) without catalysts. Ag gauze near the exit absorbs interfering acid gases, S being determined gravimetrically in the aq. extract of this. Halogens and N oxides are absorbed in external absorbents, halogens being determined titrimetrically. A. Li.

**Micro-determination of nitrogen in organic compounds by Kjeldahl's method.** E. I. Aizenschtadt (*Zavod. Lab.*, 1940, **9**, 233—234).—Reduction of  $\text{NO}_2$ - and  $\text{NO}$ -compounds by glucose often requires boiling for 3—5 hr. J. J. B.

**Semi-micro-analysis of anions.**—See A., 1943, I, 262.

**Tentative method for the determination of mono- and di-unsaturated glycerides.** A. R. S. Kartha and K. N. Menon (*Proc. Indian Acad. Sci.*, 1943, **17**, A, 114—118).—The fat or oil is oxidised by  $\text{KMnO}_4-\text{COMe}_2$  and tri-saturated glycerides are removed. The mixture of mono- (I), di- (II), and tri-azelaoglycerides, dissolved in  $\text{Et}_2\text{O}$ , is washed 5 or 6 times with 5% aq.  $\text{Na}_2\text{CO}_3$  and the extract and washings are rejected, thus removing all the monobasic acids, triazelain, and a portion of the (II). The solution is cautiously extracted with 10% aq.  $\text{K}_2\text{CO}_3$  and  $\text{H}_2\text{O}$  to extract (I) and (II). The combined extract and washings are acidified with dil.  $\text{H}_2\text{SO}_4$  to Congo-red and thoroughly extracted with  $\text{Et}_2\text{O}$ . The extract is dried over anhyd.  $\text{MgSO}_4$  and the solvent is removed completely under reduced pressure at a very low water-bath temp. The sap. val. of a portion of the residue is determined, this corresponding with a mixture of (I) and (II). The remaining residue is dissolved in  $\text{Et}_2\text{O}$  and washed alternately with  $\text{NaHCO}_3$  and  $\text{H}_2\text{O}$ ; the combined washings and extract are acidified with dil.  $\text{H}_2\text{SO}_4$  and the pure (II), after being dried, are used for determination of sap. val. The method is applied to the oils of *Mimusops elangi* and *Jatropha curcas*. H. W.

**Polarographic determination of small concentrations of aldehydes and peroxides.** M. N. Michailova and M. B. Neiman (*Zavod. Lab.*, 1940, **9**, 166—168).— $10^{-8}$  g. of  $\text{MeCHO}$  or  $\text{H}_2\text{O}_2$  can be estimated in presence of a large excess of  $\text{O}_2$  by the height of the polarographic wave. J. J. B.

**Identification and determination of  $\beta$ -phenylisopropylamine and  $\beta$ -phenylisopropylmethylamine.** G. Dultz (*Z. anal. Chem.*, 1940, **120**, 84—88).—The two compounds are detected by the use of Kofler's micro-m.p. and sublimation procedure (cf. A., 1942, II, 1). For the determination tablets are extracted with  $\text{CHCl}_3$  in presence of  $\text{NaOH}$ , excess of 0.01N- $\text{H}_2\text{SO}_4$  is added, the  $\text{CHCl}_3$  removed, and the excess of  $\text{H}_2\text{SO}_4$  titrated with  $\text{NaOH}$  using Tashiro's indicator (100 c.c. of 0.03% Me-red + 15 c.c. of 0.1% methylene-blue). F. N.

**Determination of nicotinic acid.** R. G. Martinek, E. R. Kirch, and G. L. Webster (*J. Biol. Chem.*, 1943, **149**, 245—249).—3:4:1- $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}$  is preferred to  $\text{NH}_2\text{Ph}$  etc. as chromogenic amine in the  $\text{CNBr}$ -nicotinic acid reaction; the method is less crit. with respect to pH control and time of comparison of colour; the colour reaches a max. in 5 min. and is stable for  $\leq 15$  min. A. T. P.

**Determination of nicotinic acid; modifications of the microbiological method.**—See A., 1943, III, 753.

**Determination of nicotinic acid and its amide.**—See A., 1943, III, 684.

**Determination of nicotine and nornicotine in mixtures.** L. N. Markwood (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 283—289).—Nornicotine (I) is converted into nitrosornicotine and unchanged nicotine (II) is removed by steam-distillation at pH 10. The procedure is repeated after methylation of (I) to (II) with  $\text{CH}_3\text{O}-\text{HCO}_2\text{H}$ . Recoveries of 97—98% are recorded. A. A. E.

**Spectrophotometric methods. Determination of quinine by absorption spectrophotometry.** J. Carol (*J. Assoc. Off. Agric. Chem.*, 1943, **26**, 238—241).—With the aid of a Beckmann quartz spectrophotometer quant. measurements could be made at 250.5, 318.0, and 347.5  $\mu\mu$ . Many compounds frequently present in preps. of quinine show no absorption at 347.5  $\mu\mu$ , so that separation is frequently unnecessary. Separation from aloin, podophyllin, anthraquinone derivatives, other cinchona alkaloids, and yellow dyes is necessary. A. A. E.

**Lignin. XXXVIII. Determination of lignin.** K. Freudenberg and T. Ploetz (*Ber.*, 1940, **73**, [B], 754—757).—The concn. of  $\text{H}_2\text{SO}_4$  used in determining lignin can be that which gives the min. yield, but sometimes, e.g., with linden, no such min. exists. It is thus better to use that concn. which gives a "lignin" having max. OMe content, i.e., for *Picea excelsa* and *Tilea tomentosa* 75 and for *Fagus silvatica* and *Sambucus nigra* 66.4—66.5%. The analytical method is detailed. R. S. C.

## A., II.—Organic Chemistry

NOVEMBER, 1943.

## I.—ALIPHATIC.

Modern methods of preparative organic chemistry. II. Reduction according to Meerwein and Ponndorf and oxidation according to Oppenauer. T. Bersin. III. Oxidations with lead tetra-acetate and periodic acid. R. Criegee (*Angew. Chem.*, 1940, 53, 266—271, 291, 321—326).—Reviews.

Raman spectra of meso- and dl-disubstituted butanes.—See A., 1943, I, 249.

Addition of hydrogen fluoride to halogeno-olefines. A. L. Henne and E. P. Plueddeman (*J. Amer. Chem. Soc.*, 1943, 65, 1271—1272). —CHMe:CHCl and HF at 100° give CHMeF·CH<sub>2</sub>Cl (20%), b.p. 68.5°, CHMeCl·CH<sub>2</sub>Cl (20%), CH<sub>2</sub>EtClF (10%), b.p. 46—49°, CH<sub>2</sub>EtF<sub>2</sub> (a trace), and tar. CH<sub>2</sub>Et:CHCl and HF at 65° give CHPr<sup>α</sup>ClF (10%) (identified by its b.p. 73—76°), C<sub>4</sub>H<sub>8</sub>Cl<sub>2</sub> (5%), and tar (60%; more at higher temp.). CH<sub>2</sub>EtClF is distinguished from CHMeF·CH<sub>2</sub>Cl by not reacting with Zn and by being obtained also from CH<sub>2</sub>EtCl<sub>2</sub> by HgF<sub>2</sub>. CMe<sub>2</sub>:CHCl and HF at 0° or —23° (much tar formed at higher temp.) readily give α-chloro-α-fluoroisobutane (65%), f.p. —69.3°, b.p. 82.5°, also obtained from CH<sub>2</sub>:CMe·CH<sub>2</sub>Cl owing to the isomerising effect of HF and identified by non-reaction with Zn and synthesis from CHPr<sup>β</sup>Cl<sub>2</sub> by HgF<sub>2</sub>. Results with CH<sub>2</sub>:CEtCl, CH<sub>2</sub>:CMeCl, CHMe:CMeCl, and CHMe:CEtCl confirm those of Renoll (A., 1942, II, 294); those with CPhCl:CH<sub>2</sub> are inconclusive. CH<sub>2</sub>:CCl<sub>2</sub> and HF at 65° give CMeCl<sub>2</sub>F (50%), f.p. —103.5°, b.p. 32.0°, CMeCl<sub>3</sub> (5%), and tar (10%). CH<sub>2</sub>Et:CCl<sub>2</sub> and HF at 65° give CPr<sup>α</sup>Cl<sub>2</sub>F (28%) and CPr<sup>α</sup>ClF<sub>2</sub> (15%; more at higher temp.). CMe<sub>2</sub>:CCl<sub>2</sub>, b.p. 109°, and HF at 100° give mainly CPr<sup>β</sup>Cl<sub>2</sub>F (35%), b.p. 105—109°. (CHCl)<sub>2</sub> does not react with HF. *cis*- or *trans*-CMeCl:CHCl and HF at 120° give 7 and 10%, respectively, of CMeF<sub>2</sub>·CH<sub>2</sub>Cl, f.p. —91.7°, b.p. 88.6°, with 5 and 8%, respectively, of CMeClF·CH<sub>2</sub>Cl. Similarly, CMeF:CHCl (*trans*- more readily) and HF give CMeF<sub>2</sub>·CH<sub>2</sub>Cl. CHCl:CCl<sub>2</sub>, CMeCl:CCl<sub>2</sub>, and (CCl<sub>2</sub>)<sub>2</sub> do not react with HF. CCl<sub>2</sub>:CCl·CCl<sub>3</sub> undergoes substitution in the CCl<sub>3</sub> at high temp. β-Chloro-β-fluoro-*n*-butane, f.p. —110°, b.p. 67.7°, gives CMeEtF<sub>2</sub>. R. S. C.

Acid strengths of aliphatic nitro-compounds.—See A., 1943, I, 278.

Volatile plant substances. XXIII. Presence of *n*-octan-γ-ol and its acetate in oil of pennyroyal (*Mentha pulegium*, L.). Y. R. Naves (*Helv. Chim. Acta*, 1943, 26, 1034—1036).—The isolation is described of *n*-octan-γ-ol (I), b.p. 176—176.5°/732 mm., 52—53°/2.2 mm., [α]<sub>D</sub><sup>20</sup> +7.93°, further characterised by its conversion into *n*-octan-γ-one (semicarbazone, m.p. 117—117.5°), which is oxidised to *n*-C<sub>8</sub>H<sub>11</sub>·CO<sub>2</sub>H. After removal of (I) by H<sub>3</sub>BO<sub>3</sub> the fraction gives an octyl acetate, b.p. 176—176.5°/728 mm., 74°/10 mm., *n*<sub>D</sub> —4.39°. H. W.

Production of acetylmethylcarbinol by the action of *Acetobacter suboxydans* on βγ-butylene glycol.—See A., 1943, III, 848.

βγδ-*D*-benzylidene-*D*-mannitol and its derivatives. W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, 65, 1419—1422).—*D*-Mannitol αζ-dibenzoate, PhCHO, and powdered, fused ZnCl<sub>2</sub> at room temp. give βγδ-*D*-benzylidene- (I), dimorphic, m.p. 169—170°, resolidifies, remelts 179—180°, [α]<sub>D</sub><sup>20</sup> +45.2° in CHCl<sub>3</sub> (distribution of the CHPh: uncertain), and γδ-benzylidene-*D*-mannitol αζ-dibenzoate (II), m.p. 119—120°, [α]<sub>D</sub><sup>20</sup> +31.8° in CHCl<sub>3</sub> (cf. Brigl *et al.*, A., 1932, 598); according to the conditions, yields of (I) are 24—59% and of (II) are 20—56%. PhCHO·ZnCl<sub>2</sub> at 25° converts (II) into (I). NaOMe·MeOH·CHCl<sub>3</sub> hydrolyses (II) at 5° to γδ-benzylidene-*D*-mannitol, m.p. 136—137°, [α]<sub>D</sub><sup>20</sup> +29.0° in H<sub>2</sub>O, the αβζ-tetrabenzoate, m.p. 126—127°, [α]<sub>D</sub><sup>20</sup> —27.9° in CHCl<sub>3</sub>, of which is obtained from (II) by BzCl·C<sub>6</sub>H<sub>5</sub>N at 25°. With H<sub>2</sub>SO<sub>4</sub>·Ac<sub>2</sub>O·AcOH at 25°, (I) gives *D*-mannitol βγδ-tetra-acetate αζ-dibenzoate, m.p. 126—127°, [α]<sub>D</sub><sup>20</sup> +38.9° in CHCl<sub>3</sub>, and with NaOMe·MeOH·CHCl<sub>3</sub> at 5° gives βγδ-*D*-benzylidene-*D*-mannitol, decomp. 203—205°, [α]<sub>D</sub><sup>20</sup> +76.7° in C<sub>6</sub>H<sub>5</sub>N (αζ-diacetate, m.p. 185—186°, [α]<sub>D</sub><sup>20</sup> +100.0° in CHCl<sub>3</sub>). The αζ-di-*p*-toluenesulphonate, m.p. 185—186°, [α]<sub>D</sub><sup>20</sup> +87.5° in CHCl<sub>3</sub>, thereof with H<sub>2</sub>SO<sub>4</sub>·AcOH·Ac<sub>2</sub>O gives *D*-mannitol βγδ-tetra-acetate αζ-di-*p*-toluenesulphonate (85%), m.p. 119—120°, [α]<sub>D</sub><sup>20</sup> +22.9° in CHCl<sub>3</sub>, and with NaI·COMe<sub>2</sub> at 100° gives βγδ-*D*-benzylidene-*D*-mannitol αζ-di-iodide (98%), m.p. 184—185°, [α]<sub>D</sub><sup>20</sup> +58.0° in CHCl<sub>3</sub>, reduced

by H<sub>2</sub>-Raney Ni in Ba(OMe)<sub>2</sub>·MeOH to βγδ-*D*-benzylidene-αζ-dideoxy-*D*-mannitol (96%), m.p. 159—160°, [α]<sub>D</sub><sup>20</sup> +49.5° in CHCl<sub>3</sub>, which is hydrolysed by boiling 80% AcOH to the known αζ-dideoxy-*D*-mannitol (65%), m.p. 147—148°, [α]<sub>D</sub><sup>20</sup> —21.4° in H<sub>2</sub>O. M.p. are corr. R. S. C.

Thermal decomposition of vinyl ethyl ether.—See A., 1943, I, 280.

Vitamin-E. XLI.—See A., 1943, II, 333.

New Δ<sup>θ</sup>-undecenoic acid. C. Collaud (*Helv. Chim. Acta*, 1943, 26, 1064—1069).—Hydrogenation of Δ<sup>θ</sup>-undecenoic acid in presence of Pt or Pd gives complex mixtures. In presence of Raney Ni, Na Δ<sup>θ</sup>-undecenoate in feebly alkaline solution is reduced to α-Δ<sup>θ</sup>-undecenoic acid (I), b.p. 156°/4 mm., m.p. 3—3.5°, which is shown to be homogeneous and hence appears to be a geometrical isomeride of the β-acid of Krafft *et al.* (A., 1901, i, 115). The constitution of (I) is established by ozonolysis to azelaic acid. Isomerisation of the α- to the β-acid could not be achieved. (I) is converted by successive treatments with SOCl<sub>2</sub> and NH<sub>3</sub> into α-Δ<sup>θ</sup>-undecenoamide, m.p. 84.5—85°. *p*-Phenylphenacyl α-Δ<sup>θ</sup>-undecenoate has m.p. 65—66°. H. W.

Ambrettolide and its isomerides. III. Synthesis of ζ<sub>o</sub>-dehydroxy-hexadecic acid. C. Collaud (*Helv. Chim. Acta*, 1943, 26, 1155—1162).—Δ<sup>θ</sup>-Undecenoic acid is converted by distillation with Bu<sup>α</sup>OH and C<sub>6</sub>H<sub>6</sub> containing H<sub>2</sub>SO<sub>4</sub> into its Bu<sup>α</sup> ester, b.p. 138°/2 mm., reduced by Na and boiling Bu<sup>α</sup>OH to α-Δ<sup>θ</sup>-undecenol, b.p. 113°/10 mm. (*phenylurethane*, m.p. 51—52°). This is transformed by SOCl<sub>2</sub> in CCl<sub>4</sub> containing NPhMe<sub>2</sub> into α-chloro-Δ<sup>θ</sup>-undecene, b.p. 80—82°/2 mm., converted by the successive actions of Mg and cycloheptanone in Et<sub>2</sub>O into 1-Δ<sup>θ</sup>-undecenylcycloheptan-1-ol (I), b.p. 136°/0.06 mm., which is dehydrated by distillation under 3 mm. pressure over KHSO<sub>4</sub> to Δ<sup>θ</sup>-undecenyl-Δ<sup>1</sup>-cycloheptene (II), b.p. 113°/0.1 mm. Ozonisation of (II) and treatment of the product with aq. H<sub>2</sub>O<sub>2</sub> gives ζ-ketotetradecane-αζ-dicarboxylic acid, m.p. 113—113.5°. (I) is ozonised in AcOH and the product is transformed by Zn powder into a OH-aldehyde which is hydrogenated (Raney Ni) to the non-cryst. 1-*i*-hydroxynonylcycloheptan-1-ol (III), and an isomeric diol, m.p. 98—99°, which is not dehydrated by distillation under reduced pressure over KHSO<sub>4</sub>. Under similar conditions (III) is converted into 1-*i*-hydroxynonyl-Δ<sup>1</sup>-cycloheptene, b.p. 135—136°/0.2 mm. (*phenylurethane*, m.p. 71—72°). This is ozonised and then treated successively with Zn powder and Ag<sub>2</sub>O, thus giving ζ-keto-*o*-hydroxy-hexadecic acid, m.p. 90—91°, reduced (H<sub>2</sub>-Raney Ni) to ζ<sub>o</sub>-di-hydroxyhexadecic acid, m.p. 97—98°. H. W.

Macro-molecular compounds. CCXLI. Polyesters. H. Staudinger and H. Schmidt [with S. Kautz] (*J. pr. Chem.*, 1940, [ii], 155, 129—162).—Polyesters obtained by condensing OH·[CH<sub>2</sub>]<sub>2</sub>·OH with succinic or adipic acid or OH·[CH<sub>2</sub>]<sub>6</sub>·OH (I) with CO<sub>2</sub>H·[CH<sub>2</sub>]<sub>14</sub>·CO<sub>2</sub>H at high temp. are too insol. for investigation. CHMe(CH<sub>2</sub>·OH)<sub>2</sub> and sebacic acid (II) give viscous polyesters. Polyesters from (I) and (II) at 200° or 220° contain terminal CO<sub>2</sub>H and CH<sub>2</sub>·OH, determined by titration and acetylation, respectively. CH<sub>2</sub>N<sub>2</sub> then gives Me esters, which can be acetylated by Ac<sub>2</sub>O·C<sub>6</sub>H<sub>5</sub>N, both reactions occurring without change of the degree of polymerisation. Acetylation of the original polyesters leads to further condensation, but esterification of these products by CH<sub>2</sub>N<sub>2</sub> causes no further increase in the degree of polymerisation. Me<sub>2</sub> sebacate (III) and (I) with a trace of NaOMe at ~200° give polyesters, which are acetylated without further condensation. For all these products the same degree of polymerisation is indicated by means of η in C<sub>6</sub>H<sub>6</sub> or CCl<sub>4</sub>, cryoscopy in 2-C<sub>10</sub>H<sub>7</sub>Me, or analyses; these polyesters are straight-chain polymerides containing 95—350 units. Heating (I) and (II) at 250°/high vac. for 10 days gives a little C<sub>8</sub>H<sub>18</sub> (? C<sub>8</sub>H<sub>18</sub>) and highly polymerised esters, the mol. wt. ranging from 8760 (determined cryoscopically) to 20,700 (determined by osmosis in CHCl<sub>3</sub>); methylation and then acetylation each causes condensation; in all cases η gives lower vals. for the mol. wt. and determination of CO<sub>2</sub>H and CH<sub>2</sub>·OH gives still lower vals.; these esters thus have branched chains containing ...CH<sub>2</sub>·CH(CO·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H)·CO<sub>2</sub>·CH... Adding NaOEt to (I) and (III) at ~150° gives three-dimensional solid products, insol. in org. solvents and swelling in CHCl<sub>3</sub> or C<sub>6</sub>H<sub>6</sub>; extracting these products with C<sub>6</sub>H<sub>6</sub> gives ~4% of mixed products, having mol. wt. (osmosis) up to 16,100, which are branched (since

$\eta$  and analysis give lower "mol. wts.") and have very low OMe contents, so that they probably contain mainly  $\cdots\text{CH}_2\cdot\text{CH}\cdot\text{CH}(\text{O}[\text{CH}_2]_6\cdot\text{OH})_2\cdot\text{COCl}\cdot[\text{CH}_2]_6\cdot\text{COCl}$  and (I) at 180° or 200° give branched-chain products, which contain  $\text{CO}_2\text{H}$  and also give low "mol. wts." by  $\eta$  or analysis.  $(\text{CH}_2\cdot\text{OH})_2$  and (I) give polyesters which are methylated and then acetylated without condensation; mol. wts. determined by cryoscopy exceed (by 18—27%) those determined by  $\eta$ , probably owing to crumpling of the chain (Fuller, A., 1937, I, 172; 1939, I, 601). The extent of ring-crumpling in the other esters is unknown and obscures the results. During determination of OAc in the products by  $\text{KOH}\cdot\text{MeOH}$  air must be rigidly excluded to avoid formation of  $\text{HCO}_2\text{H}$ . R. S. C.

**Change of *d*-, into meso-tartaric acid by pancreas.**—See A., 1943, III, 769.

**Aldol condensation. I. Detection of carbonyl groups in aldols by means of Raman spectra.** R. H. Saunders, M. J. Murray, F. F. Cleveland, and V. I. Komarewsky (*J. Amer. Chem. Soc.*, 1943, 65, 1309—1311).—Raman spectra are recorded for acet- (I), propion- (II), and butyr-aldol (III) (cf. Hibben, A., 1932, 983; Backés, A., 1938, II, 392). Only (III) shows a CHO line which disappears in a few days. There is no evidence of C:C. The change of (I) and (II) from mobile to viscous liquids is thus not due to gradual disappearance of CO functions. R. S. C.

**Essential steps in the catalytic condensation of aldehydes; synthesis of glycol esters.** M. S. Kulpinski and F. F. Nord (*J. Org. Chem.*, 1943, 8, 256—270).—The catalytic condensation of the dissimilar aldehydes,  $\text{Pr}^a\text{CHO}$  and  $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ , to yield an unsaturated glycol ester represents a second form of the "crossed" Cannizzaro reaction, the *cis*- and *trans*-conjugated aldehydes thus obtained representing an interesting example of such isomerides. Co-ordination catalysts permit a trimeric autocondensation of saturated aldehydes; this is generally applicable to  $\alpha\text{-CH}_2$  aldehydes and provides a convenient method for the synthesis of glycol esters of this series. Simple alkoxides lead only to dimeric products whereas complex catalysts can bring about trimerisation. Failure to obtain glycol esters as the main products in the case of  $\alpha$ -alkylaldehydes with the co-ordination catalysts is due to the limiting factors imposed on the primary stage of the condensation, *i.e.*, aldolisation. The similarity of behaviour in this instance between the simple and the complex alkoxides originates in the bifunctional nature of the latter. The complex alkoxides do not differ qualitatively in their action.  $\text{Mg}[\text{Al}(\text{OEt})_4]_2$  appears to be a better condensing agent than  $\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2$  or  $\text{Mg}[\text{Al}(\text{OBu}^t)_4]_2$  but it is more difficult to prepare.  $\text{Mg}[\text{Al}(\text{OEt})_4]_2$  converts a mixture of  $\text{Pr}^a\text{CHO}$  and  $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$  into  $\beta$ -ethyl- $\Delta^8$ -hexene- $\alpha$ -diol monobutyrate, b.p. 104.5—105.5°/2 mm. (acetate, b.p. 89—90°/1 mm.), hydrogenated to  $\beta$ -ethylhexane- $\alpha$ -diol monobutyrate (I), b.p. 100—102°/0.5 mm., which is hydrolysed to  $\beta$ -ethylhexane- $\alpha$ -diol (II), b.p. 88—90°/1 mm., and *cis*-, b.p. 42—43°/2 mm., and *trans*- $\alpha$ -ethyl- $\Delta^8$ -hexadienal, b.p. 44—45°/2 mm. (semicarbazones, m.p. 185—186° and 201—202°; 2:4-dinitrophenylhydrazones, m.p. 136—137° and 187.5—188.5°). (I) is also obtained from  $\text{Pr}^a\text{CHO}$  alone under the influence of  $\text{Mg}[\text{Al}(\text{OEt})_4]_2$ ,  $\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2$ , or  $\text{Mg}[\text{Al}(\text{OBu}^t)_4]_2$  whereas  $\text{Pr}^a\text{CO}_2\text{Bu}$  is obtained under the influence of  $\text{Al}(\text{OEt})_3$  or  $\text{Al}(\text{OPr}^i)_3$ . (II) gives a diacetate, b.p. 87—88°/1 mm.  $\text{MeCHO}$  and  $\text{Mg}[\text{Al}(\text{OAlk})_4]_2$  afford  $\text{EtOAc}$ ,  $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ , paracetaldehyde, metaldehyde, and butane- $\alpha$ -diol monoacetate, b.p. 87—89°/13 mm. (corresponding diacetate, b.p. 92—94°/13 mm.). Similarly  $\text{EtCHO}$  affords  $\alpha$ -methyl- $\Delta^8$ -pentenal (2:4-dinitrophenylhydrazone, m.p. 159.5°) and  $\beta$ -methylpentane- $\alpha$ -diol monopropionate, b.p. 92—94°/2 mm. (acetate, b.p. 71—72°/0.5 mm.), hydrolysed to the diol, b.p. 85—86°/1 mm.  $\text{Bu}^t\text{CHO}$  yields  $\zeta$ -methyl- $\beta$ -isopropylhexane- $\alpha$ -diol monoisovalerate, b.p. 137—139°/1 mm. (acetate, b.p. 126—128°/1 mm.), whence the (impure) diol, b.p. 105—106°/1 mm. In like manner  $\text{Bu}^a\text{CHO}$  affords  $\beta$ -propylheptane- $\alpha$ -diol monovalerate, b.p. 138—139°/1 mm. (acetate, b.p. 135—137°/1 mm.), and the diol, b.p. 107—108°/1 mm.,  $n\text{-C}_5\text{H}_{11}\cdot\text{CHO}$  gives  $\beta$ -butyloctane- $\alpha$ -diol monohexanoate, b.p. 750—752°/1 mm. (monoacetate, b.p. 132—134°/0.5 mm.), and the diol, b.p. 128—129°/1 mm., and  $n\text{-C}_6\text{H}_{13}\cdot\text{CHO}$  gives  $\beta$ -amylnonane- $\alpha$ -diol monoheptanoate, b.p. 167—170°/0.5 mm. (acetate, b.p. 160—164°/1 mm.), and the diol, b.p. 125—127°/0.5 mm. With  $\text{Pr}^i\text{CHO}$  the complex alkoxides afford mainly  $\text{Pr}^i\text{CO}_2\text{Bu}^i$  with small amounts of  $\beta\beta\delta$ -trimethylpentane- $\alpha$ -diol monoisobutyrate, b.p. 85—86°/0.5 mm. (acetate, b.p. 91—93°/2 mm.), hydrolysed to the (impure) diol, b.p. 81—82°/1 mm.  $\text{CHEt}_2\cdot\text{CHO}$  gives preponderatingly  $\beta$ -ethylbutyl  $\alpha$ -ethylbutyrate, b.p. 100—102°/14 mm., identified by hydrolysis to  $\text{CHEt}_2\cdot\text{CH}_2\cdot\text{OH}$  (3:5-dinitrobenzoate, m.p. 50°) and  $\text{CHEt}_2\cdot\text{CO}_2\text{H}$  (amide, m.p. 125°) with small amounts of  $\beta\beta\delta$ -triethylhexane- $\alpha$ -diol monoethylbutyrate, b.p. 127—130°/1 mm., whence the diol. In all cases  $\text{CHEtBu}^a\cdot\text{CHO}$  gives exclusively  $\beta$ -ethylhexyl  $\alpha$ -ethylhexanoate, b.p. 112—116°/1 mm., hydrolysed to  $\beta$ -ethylhexanol (1-naphthylurethane, m.p. 59—60°) and  $\beta$ -ethylhexoic acid (amide, m.p. 102°). H. W.

**Direct reduction of certain carboxylic acids to aldehydes, and preparation of undecaldehyde by a modified Blaise reaction.** R. R. Davies and H. H. Hodgson (*J.S.C.I.*, 1943, 62, 128).—The direct reduction of salicylic, *n*-butyric, nonoic, and lauric acid by

$\text{Na}\cdot\text{Hg}$  produced only poor yields of the corresponding aldehydes, which were hardly improved by the use of dispersing agents. The Blaise reaction has been modified to produce a 62.3% yield of  $\text{C}_{10}\text{H}_{21}\cdot\text{CHO}$  from lauric acid.

**Tertiary alkyl primary amines,  $\text{CRR}'\text{R}''\cdot\text{NH}_2$ . III.** H. R. Henze and T. R. Thompson (*J. Amer. Chem. Soc.*, 1943, 65, 1422—1425; cf. A., 1943, II, 153).— $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{MgBr}$  (I) and  $\text{OEt}\cdot\text{CHMe}\cdot\text{CN}$  (II) (prep. from  $\text{CHMeCl}\cdot\text{OEt}$  by  $\text{CuCN}\cdot\text{C}_6\text{H}_6$ ; 51% yield), b.p. 129—130°/751 mm., give  $\delta$ -amino- $\delta$ - $\alpha'$ -ethoxyethyl- $\Delta^8$ -*n*-heptadiene (35%), b.p. 198—198.5°/751 mm., 70°/5 mm. (picrate, m.p. 103°, prepared in  $\text{SO}_2\cdot\text{H}_2\text{O}$ ), hydrogenated ( $\text{PtO}_2$ ;  $\text{COMe}_2$ ) to  $\delta$ -amino- $\delta$ - $\alpha'$ -ethoxyethyl-*n*-heptane (94.5%), b.p. 56°/2 mm. (picrate, m.p. 110.5°).  $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{CN}$  (prep. from  $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{Cl}$  by  $\text{NaCN}$ ) with  $\text{SOCl}_2\cdot\text{CHCl}_3$  gives  $\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{CN}$  (60%), b.p. 175°/747 mm., converted by  $\text{NaOEt}\cdot\text{EtOH}$  at 0° and then the b.p. into  $\text{OEt}\cdot[\text{CH}_2]_2\cdot\text{CN}$  (III) (57.5%), b.p. 78°/25 mm., which with (I) yields  $\delta$ -amino- $\delta$ - $\beta'$ -ethoxyethyl- $\Delta^8$ -*n*-heptadiene (33%), b.p. 95°/5 mm. (picrate, m.p. 91°), and thence *n*-heptane, b.p. 100°/10 mm. (picrate, m.p. 99.5°). Adding (I) to the product from (II) and  $\text{MgPr}^a\text{Br}$  gives  $\delta$ -amino- $\delta$ - $\alpha'$ -ethoxyethyl- $\Delta^8$ -*n*-heptene (40%), b.p. 78°/3 mm. (picrate, m.p. 103°), and a small amount of  $\text{OEt}\cdot\text{CHMe}\cdot\text{COPr}^a$  (IV) (semicarbazone, m.p. 124.5°); this reaction fails with (III). Adding (II) to  $\text{MgPr}^a\text{Br}$  in  $\text{Et}_2\text{O}$ , replacing the  $\text{Et}_2\text{O}$  by  $\text{Bu}^a_2\text{O}$ , and heating gives 28% of (IV), b.p. 163—164°/759 mm., and a smaller amount of  $\delta$ - $\alpha'$ -ethoxyethyl-*n*-heptan- $\delta$ -ol, b.p. 203—205°/759 mm.; in boiling  $\text{Et}_2\text{O}$ , 50% of (IV) is obtained; (III) does not undergo this reaction. Adding (I) to the product from  $\text{MgMeI}$  and  $\text{OPr}^a\cdot\text{CH}_2\cdot\text{CN}$  in  $\text{Et}_2\text{O}$  gives  $\beta$ -amino- $\alpha$ -*n*-propoxy- $\beta$ -methyl- $\Delta^8$ -*n*-pentene (51%), b.p. 100°/100 mm. (picrate, m.p. 110°), and some  $\text{OPr}^a\cdot\text{CH}_2\cdot\text{COMe}$  (semicarbazone, m.p. 75°);  $\text{H}_2\cdot\text{PtO}_2$  in  $\text{EtOH}$  then yields  $\beta$ -amino- $\alpha$ -*n*-propoxy- $\beta$ -methyl-*n*-pentane, b.p. 105—106°/100 mm. (picrate, m.p. 95°). Adding  $\text{iso-C}_5\text{H}_{11}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CN}$  to  $\text{MgMeI}\cdot\text{Et}_2\text{O}$  and then to (I)- $\text{Et}_2\text{O}$  gives  $\beta$ -amino- $\alpha$ -isoamyloxy- $\beta$ -methyl- $\Delta^8$ -*n*-pentene (65%), b.p. 89—90°/8 mm. (picrate, m.p. 104°),  $\text{iso-C}_5\text{H}_{11}\cdot\text{O}\cdot\text{CH}_2\cdot\text{COMe}$  (semicarbazone, m.p. 60°), and  $\text{iso-C}_5\text{H}_{11}\cdot\text{OH}$  (3:5-dinitrobenzoate, m.p. 61°).  $\beta$ -Amino- $\alpha$ -isoamyloxy- $\beta$ -methyl-*n*-pentane, b.p. 97°/8 mm. (picrate, m.p. 86°), is also prepared. M.p. are corr. The amines prepared slightly lower the blood pressure of pithed cats. R. S. C.

**Hydroxyalkylamino-acids.** W. Cocker (*J.C.S.*, 1943, 373—378).—Allyl bromide, 3*N*- $\text{NaOH}$ , and the appropriate arylsulphonylglycine at 100° afford *N*-benzenesulphonyl- (I), m.p. 107°, and *N*-*p*-toluenesulphonyl- (II), m.p. 109—110°, *N*-allylglycine which rapidly decolorise  $\text{Br}\cdot\text{H}_2\text{O}$  and alkaline  $\text{KMnO}_4$ . Ozonisation of (II) leads to *N*-*p*-toluenesulphonyl-*N*-aldehydomethylglycine, identified as the 2:4-dinitrophenylhydrazone, m.p. 173—174°. (I) is hydrolysed by 60%  $\text{H}_2\text{SO}_4$  at 125° to *dl*-*N*- $\beta$ -hydroxypropylglycine (III), m.p. 194—195° (decomp.), converted by  $\text{PhSO}_2\text{Cl}$  in alkaline solution followed by acidification into *N*-benzenesulphonyl-6-methyl-2-morpholine (IV), m.p. 128—128.5°. *N*-*p*-Toluenesulphonyl-*N*- $\beta$ -hydroxypropylglycine (V), m.p. 138—139°, passes at 120°/vac. or when treated with  $\text{Ac}_2\text{O}$ ,  $\text{SOCl}_2$ , or boiling  $\text{C}_6\text{H}_6$  into *N*-*p*-toluenesulphonyl-6-methyl-2-morpholine, m.p. 92—93°. (I) and (II) are converted by conc.  $\text{H}_2\text{SO}_4$  into (IV) and (V) respectively.  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NH}_2$  [phenylcarbamyl derivative, (?)  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , m.p. 108—109°, and its phenylurethane, m.p. 180—181°] and  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  yield (III). Oxidation of (III) by I and  $\text{Na}_2\text{CO}_3$  gives  $\text{CHI}_3$  as sole cryst. compound.  $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , methylallyl chloride, and 3*N*- $\text{NaOH}$  at 100° afford *N*-benzenesulphonyl-*N*- $\beta$ -methylallylglycine (VI), m.p. 91—92°. *N*-*p*-Toluenesulphonyl-*N*- $\beta$ -methylallylglycine (VII), m.p. 109—110° (also +  $\text{C}_6\text{H}_6$ ), is transformed by  $\text{HCl}\cdot\text{EtOH}$  into *Et* *N*-*p*-toluenesulphonyl-*N*- $\beta$ -chloroisobutylaminoacetate, m.p. 67.5—68°. (VI) and conc.  $\text{H}_2\text{SO}_4$  afford *N*-benzenesulphonyl-6:6-dimethyl-2-morpholine (VIII), m.p. 134—135°, and  $\text{Pr}^i\text{CHO}$ ; (VII) similarly gives *N*-*p*-toluenesulphonyl-6:6-dimethyl-2-morpholine, m.p. 133—134°. Ozonolysis of (VI) leads to *N*-benzenesulphonyl-*N*-acetonylglycine, m.p. 123° (2:4-dinitrophenylhydrazone).  $\text{Pr}^i\text{CHO}$  is formed by hydrolysis of (VIII) by boiling 60%  $\text{H}_2\text{SO}_4$ . *N*-Mesitylenesulphonyl-*N*- $\beta$ -methylallylglycine, m.p. 117—118°, best obtained from *Et* mesitylenesulphonamidoacetate, m.p. 43—44°, is hydrolysed by boiling  $\text{AcOH}$ -conc.  $\text{HCl}$  to *N*- $\beta$ -hydroxyisobutylglycine, m.p. 176° (decomp.), also prepared from  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{NH}_2$  and  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ .  $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$  and  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br}$  give a mixture from which *N*-benzenesulphonyl-3:6-dimethyl-2-morpholine; *N*-benzenesulphonyl-*N*-allylalanine, m.p. 95°, is obtained by hydrolysis of the product from  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$  and *Et* benzenesulphonyl- $\alpha$ -aminopropionate, m.p. 61—62°, in  $\text{NaOEt}\cdot\text{EtOH}$ .  $\beta$ -Hydroxypropylalanine, m.p. 214°, is derived from  $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$  and  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NH}_2$  in  $\text{EtOH}$ . *Et* *p*-toluenesulphonyl- $\alpha$ -aminopropionate, m.p. 66—67°, and mesitylenesulphonylalanine, m.p. 155—156°, are incidentally described.  $\text{Br}$  in  $\text{CHCl}_3$  converts the requisite unsaturated compound into *N*-benzenesulphonyl-*N*- $\beta$ -dibromopropylglycine (IX), m.p. 117—118° (*Me*, m.p. 101—102°, and *Et*, m.p. 72°, ester), and *N*-*p*-toluenesulphonyl-*N*- $\beta$ -dibromopropylglycine (X), m.p. 127—128°. (IX) is reduced ( $\text{H}_2$ -Raney Ni in  $\text{MeOH}$ ) to  $\text{SO}_2\text{Ph}\cdot\text{NHPr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  whereas  $\text{Zn}$  dust and glacial  $\text{AcOH}$  at 100° reduce (X) to (II). (X) is hydrolysed to  $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$ , *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and a compound, m.p. 193°. Glycine, *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ , and *N*- $\text{NaOH}$  afford *N*-*m*-nitrobenzenesulphonylglycine, m.p. 149—150°;

the *Et* ester, m.p. 122°, is transformed by  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$  and  $\text{NaOEt}$  in *EtOH* into *Et* *N*-*m*-nitrobenzenesulphonyl-*N*-allylaminoacetate, m.p. 57.5—58° (dibromide, m.p. 91—91.5°). H. W.

**Growth effects of  $\alpha$ -methyl homologues of pantothenic acid and  $\beta$ -alanine.** M. A. Pollack (*J. Amer. Chem. Soc.*, 1943, **65**, 1335—1339).— $\text{CN}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$  (prep. from  $\text{CHMeCl}\cdot\text{CO}_2\text{Na}$  by aq.  $\text{NaCN}$  at 85—100°, followed by evaporation and esterification), b.p. 77°/9.5 mm., is hydrogenated ( $\text{PtO}_2\text{--H}_2\text{SO}_4\text{--AcOH}$ ; 530 lb.) and the product is repeatedly evaporated with addition of water. The *Na* salt of the resulting  $\alpha$ -methyl- $\beta$ -alanine (73%), m.p. 181—182°, with *l*- $\alpha$ -hydroxy- $\beta$ -dimethyl- $\gamma$ -butyrolactone at 108° or in boiling *EtOH*- $\text{Pr}^i\text{OH}$  gives *Na*  $\alpha$ -methylpantothenate. For biological results see A., 1943, III, 847. R. S. C.

***dl*-Ethylalanine.**—See A., 1943, III, 768.

**Effect of *N*-methylation on structure and properties of linear polyamides.**—See A., 1943, I, 251.

**Higher alkyl thiocyanates.** T. Wagner-Jauregg, H. Arnold, and H. Hippchen (*J. pr. Chem.*, 1940, [ii], **155**, 216—224).—The following thiocyanates are prepared from the respective alkyl bromide and  $\text{NaCNS}\cdot 2\text{H}_2\text{O}$  in aq.  $\text{COMe}_2$  (reflux and then autoclave at 80°) or *EtOH* (reflux) (cf. Allen, A., 1935, 479): *oleyl*, b.p. 205—210°/0.1 mm., *elaidyl*, b.p. 198—199°/0.1 mm., *linoleyl*, b.p. 202°/0.15 mm., *hydrocarpyl*, b.p. 190—210°/0.5 mm., and its  $\text{H}_2$ -derivative, b.p. 205—215°/0.3 mm., *cholesteryl*, m.p. 129—130°, *cinnamyl* (I), b.p. 140—150°/0.3 mm., *cetyl*, b.p. 190—195°/0.2 mm., and *undecyl*, b.p. 140—150°/0.1 mm., thiocyanate. *Cinnamyl* bromide and (I) or  $\text{NaCNS}\cdot 2\text{H}_2\text{O}$  in boiling 99% *EtOH* yield *cinnamyl cinnamyl-aminothioformate*,  $\text{SR}\cdot\text{CO}\cdot\text{NHR}$  ( $\text{R} = \text{CH}_2\cdot\text{CH}\cdot\text{CHPh}$ ), m.p. 111—112°. A. T. P.

## II.—SUGARS AND GLUCOSIDES.

**Complex mutarotation of *d*-galactose.** R. E. Rundle and B. C. Hendricks (*J. Physical Chem.*, 1943, **47**, 364—369).—Published data for the mutarotation of  $\alpha$ - and  $\beta$ -*d*-galactoses at 20° and 0° have been used to calculate the course of "thermal mutarotation" which occurs when an equilibrium solution is rapidly cooled. The course of the mutarotation of a pseudo-equilibrium mixture of  $\alpha$ - and  $\beta$ -*d*-galactoses at 0° has been similarly calc. The calc. results agree well with published data. The mechanism of mutarotation is discussed. The mechanism of Smith and Lowry (A., 1928, 510) is regarded as of more general application than that of Isbell and Pigman (A., 1937, II, 177, 275; 1938, II, 349). C. R. H.

**Behaviour of lactose in alkaline solution.** IV. B. Bleyer and A. Schloemer (*Biochem. Z.*, 1940, **306**, 155—160; cf. A., 1923, i, 1180).— $[\alpha]$  of 5 and 10% aq.  $\alpha$ -lactose at first increases, then decreases, as a result of addition of aq.  $\text{NaOH}$  (0.20—20.0%). Subsequent neutralisation increases  $[\alpha]$  to an extent  $\propto$  to the conc. of  $\text{NaOH}$  used to produce the decrease. The changes are explained by supposing concurrent, complete degradation by  $\text{NaOH}$  and production of substances (e.g.,  $\alpha$ -galactose, *d*-sorbose) having  $[\alpha] >$  that of  $\alpha$ -lactose. Neutralisation increases  $[\alpha]$  by altering the equilibrium between  $\alpha$ - and  $\beta$ -forms of the intermediate products. W. McC.

**Enzymes present in highly purified invertase preparations. Fructofuranosidases, galactosidases, glucosidases, and mannosidases.**—See A., 1943, III, 844.

**Orientation in stretched films of amylose triacetate.**—See A., 1943, I, 251.

**Sclerotiose, polysaccharide metabolite of *Penicillium sclerotiorum*, van Beyma.** V. J. Albericci, T. P. Curtin, and D. Reilly (*Biochem. J.*, 1943, **37**, 243—246).—The metabolic products of *P. sclerotiorum* include a polyglucose, *sclerotiose*, m.p. 290—300°, becomes brown at 260°,  $[\alpha]_D^{20} + 244^\circ$  in 6%  $\text{NaOH}$ ,  $[\alpha]_D^{90} + 284^\circ$  in  $\text{HCO}\cdot\text{NH}_2$  [nitrate,  $\text{C}_3\text{H}_3\text{O}_{11}(\text{NO}_3)_9$ , m.p. 200° (decomp.)]; *undecanitate*, m.p. 132° (decomp.); *diacetate*,  $\text{C}_6\text{H}_8\text{O}_3(\text{OAc})_2$ ; *triacetate*,  $\text{C}_6\text{H}_7\text{O}_2(\text{OAc})_3$ , m.p. 165—168° (decomp.),  $[\alpha]_D + 205.7^\circ$  in  $\text{CHCl}_3$ ; (?) *tribenzoate*] (cf. A., 1943, III, 846). P. G. M.

**Action of macerans amylase on the fractions from starch.** E. J. Wilson, jun., T. J. Schoch, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1380—1383).—Starch is fractionated by  $\text{BuOH}$ -*iso*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$  by use of an ordinary or super-centrifuge. The pptd. fractions from maize or potato starch with *B. macerans* amylase yield more Schardinger dextrans and less limit dextrans than do the original starches; for the non-pptd. fractions these proportions are reversed. Waxy maize starch resembles the non-pptd. fractions. Formation of insol. " $\gamma$ -amylose" does not occur under proper conditions; its formation observed by Kerr (A., 1943, II, 156, 157) is due to the conditions used. Alkali-lability increases during the enzymolysis. Schardinger  $\alpha$ - and  $\beta$ -dextrans are stable to alkali, but limit dextrans are unstable. R. S. C.

**Macro-molecular compounds. CCXXXVIII. Lower and macro-molecular chemistry.** H. Staudinger (*J. pr. Chem.*, 1940, [ii], **155**, 1—12).—The scope and general properties of compounds of very high mol. wt. are reviewed. R. S. C.

**X-Ray studies of reactions of cellulose in non-aqueous systems.**

**II. Interaction of cellulose and primary amines.** W. E. Davis, A. J. Barry, F. C. Peterson, and A. J. King (*J. Amer. Chem. Soc.*, 1943, **65**, 1294—1299; cf. A., 1936, 458).—Ramie cellulose swells in  $\text{NH}_2\text{R}$  if  $\text{R} = \text{Me}$ , *Et*, or *Pr*, but only after pre-swelling in  $\text{NH}_3$  if  $\text{R} = \text{Bu}-\text{C}_7\text{H}_{15}$ . X-Ray diffraction spectra are recorded for the products. The 101 lines retain their intensity but show a progressive increase in interplanar distance from 14.67 ( $\text{R} = \text{Me}$ ) to 28.74 Å. ( $\text{R} = \text{C}_7\text{H}_{15}$ ) (cf. 10.6 Å. if  $\text{R} = \text{H}$ ; *loc. cit.*; also Hess *et al.*, A., 1937, II, 401, and Clark *et al.*, *ibid.*, 447). The other lines are little changed. The structure thus changes to a diamond of progressively increasing length but const. width. The increase in length corresponds to insertion of 2  $\text{NH}_2\text{R}$  between cellulose units. For higher alkyl this insertion cannot occur for steric reasons; hence the necessity for pre-swelling in  $\text{NH}_3$ . Swelling occurs by creation of  $\text{O}\cdots\text{H}\cdots\text{N}$  bridges between the cellulose and  $\text{NH}_2\text{R}$ . No swelling occurs in  $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{NH}_2$  because this would change the surface of the cellulose; it does, however, occur in  $(\text{CH}_2\cdot\text{NH}_2)_2$  as expected on this hypothesis. R. S. C.

**Macro-molecular compounds. CCXLII. Native and precipitated celluloses and their nitrates.** H. Staudinger and A. W. Sohn (*J. pr. Chem.*, 1940, [ii], **155**, 177—215; cf. A., 1942, II, 353).—Nitration of native fibre cellulose with  $\text{HNO}_3\text{--H}_3\text{PO}_4$  gives nitrates of the same degree of polymerisation (D.P.) whether or not  $\text{KClO}_3$  is added to the nitration mixture. The effect of dissolution, nitration, oxidation, etc. on D.P. of celluloses and cellulose esters is discussed. The D.P. of cellulose esters is found by dissolving in conc.  $\text{H}_3\text{PO}_4$ , pptg. with  $\text{H}_2\text{O}$  at 0°, dissolving the ppt. in Schweitzer's reagent, and determining  $\eta$ . In this treatment,  $\text{H}_3\text{PO}_4$  hydrolyses ~50% of the ester groups and, when oxycellulose esters are examined, some of the glucosidic linkings are broken. With normal celluloses, pptn. from Schweitzer's reagent or treatment with  $\text{H}_3\text{PO}_4$  has no effect on D.P. Ramie is converted into oxycellulose esters by  $\text{Cr}_2\text{O}_7$  or  $\text{H}_2\text{C}_2\text{O}_4$ , the properties of the product being similar to those of oxycellulose ester from cotton. Technical sulphite pulp, which has a high ester val., and ramie oxycellulose ester are converted into normal cellulose by pptn. from solution in Schweitzer's reagent. The average D.P. of oxycellulose esters in Schweitzer's reagent does not change after keeping for 4 months at 20° and 60% R.H., but the ester groups are partly hydrolysed. The nitrates of cellulose esters are more stable than are the oxycellulose esters. Data for the degradation of nitrates of normal cellulose and of oxycellulose ester at 105° are tabulated and discussed. Oxycellulose esters with a high ester val. readily yield sol. acetates on treatment with 90%  $\text{H}_3\text{PO}_4$  (which reduces the ester val. and produces swelling) followed by treatment with  $\text{Ac}_2\text{O}\text{--C}_5\text{H}_5\text{N}$  at 60°; the product has a higher D.P. than had the initial material. Hydrolysis of these acetates gives oxycellulose esters of D.P. approx. the same as the original oxycellulose ester. When degraded cellulose (D.P. ~1000), which gives a nitrate of considerably higher D.P. (~1400), is treated in 89%  $\text{H}_3\text{PO}_4$ , the product gives a nitrate (or acetate) of approx. equal D.P. (~900). Data are given for the tensile strength of normal celluloses and oxycellulose esters; the quality of fibres of the latter is indicated by the D.P. of the nitrates in  $\text{COMe}_2$ . The tenacity of fibres of oxycellulose esters is approx. the same as that of fibres of normal celluloses of the same D.P., although the former are not stable to, e.g., washing with  $\text{H}_2\text{O}$ . The above results are discussed in relation to previously published data. F. O. H.

**Macro-molecular compounds. CCXXXIX. Constitution of wood polyoses.** E. Husemann (*J. pr. Chem.*, 1940, [ii], **155**, 13—64).—Treating washed wheat straw with 0.25% aq.  $\text{ClO}_2$  containing 2% of  $\text{C}_5\text{H}_5\text{N}$  for 18 days and then with 6% aq.  $\text{NaOH}$  in absence of air and light, filtering, treating the filtrate with  $\text{MeOH}$  and  $\text{AcOH}$ , washing the ppt. and purifying it by pptn. from 6%  $\text{NaOH}$  by  $\text{MeOH}$  gives xylan-I (I),  $[\alpha]_D - 87^\circ$  in 6%  $\text{NaOH}$ , sol. in Schweitzer's reagent and  $\text{NaOH}$  at room temp. and in  $\text{H}_2\text{O}$  and  $\text{HCO}\cdot\text{NH}_2$  at 90°; its acetate and nitrate are insol.; with  $\text{Me}_2\text{SO}_4\text{--KOH--N}_2$  it gives a Me ether (II) (32%  $\text{OMe}$ ) and thence ( $\text{Ac}_2\text{O}\text{--C}_5\text{H}_5\text{N}$ ) a Me ether acetate (III). Osmotic measurements of (I) in  $\text{HCO}\cdot\text{NH}_2$ , of (II) in  $\text{CHCl}_3$  or  $\text{H}_2\text{O}$ , and of (III) in  $\text{COMe}_2$  indicate degrees of polymerisation 119, 113, and 123, respectively. Treating the straw directly with 8%  $\text{NaOH}$  and methylating the crude product gives a Me ether and Me ether acetate (30—31%  $\text{OMe}$ ; 8%  $\text{Ac}$ );  $\text{CH}_2\text{PhCl--30\% NaOH}$  and then acetylation give a  $\text{CH}_2\text{Ph}$  ether acetate (~8.5%  $\text{Ac}$ ); these products have (osmosis) degrees of polymerisation 151—152, 146, and 145, respectively. Thus,  $\text{ClO}_2$  causes considerable degradation. All these products obey Staudinger's law for  $\eta$ , showing linear configuration;  $K_\eta$  are  $4.2\text{--}8.0 \times 10^{-4}$ , indicating absence of much chain-branching. Extracting beech wood with 8%  $\text{NaOH}$  and purifying the product with 0.2%  $\text{ClO}_2$  gives ~6—8% of a xylan,  $[\alpha]_D - 87^\circ$ ; treating the residue for a short time with  $\text{ClO}_2\text{--H}_2\text{O}\text{--C}_5\text{H}_5\text{N}$  and then with 8%  $\text{NaOH}$  gives a further 8% of xylan,  $[\alpha]_D - 83^\circ$  in 6%  $\text{NaOH}$ ; these products and their  $\text{CH}_2\text{Ph}$  ether acetates have degrees of polymerisation 144—157 and  $K_\eta$  (Staudinger's equation)  $4.4\text{--}6.8 \times 10^{-4}$ . Fractional pptn. of the xylylans and a Me ether shows that <94% has homogeneous chain-length; for the  $\text{CH}_2\text{Ph}$  ether acetate 70—80% of homogeneity is indicated. The xylylans thus are linear products from uniformly

~150 xylose units; the facts that xylans are more sol. than cellulose although the  $K_m$  are similar indicates a regular series of very short side-chains. Treating pine wood with 0.25% aq.  $\text{ClO}_2 + \text{C}_5\text{H}_5\text{N}$  and then with 8% NaOH, purifying the product by  $\text{ClO}_2$ , and finally fractionally pptg. from 6% NaOH by MeOH gives two fractions having  $[\alpha]_D -20^\circ$  to  $-25^\circ$  and then 5 fractions having  $[\alpha]_D -42^\circ$  to  $-44^\circ$  in NaOH and similar  $\eta$ . These last fractions have (osmosis in 0.1N- $\text{CaCl}_2$ ) a degree of polymerisation 150; they give a  $\text{CH}_2\text{Ph}$  ether acetate for which the degree of polymerisation (osmosis in  $\text{CHCl}_3$ ) is 147.  $K_m$  (Staudinger's equation) indicates a linear mol., although variation from 3.9 to 7.1 according to the solvent is unexplained. Extracting *Larix occidentalis* with  $\text{H}_2\text{O}-\text{N}_2$  at room temp., pptg. by MeOH, and purifying the product by  $\text{ClO}_2$  and repptn. gives an arabogalactan (IV) having a degree of polymerisation 222;  $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$  at  $60^\circ$  gives a degraded acetate (V) (43.9% Ac; degree of polymerisation 75—81), but at  $20^\circ$  gives an acetate (VI) (33.44% Ac) having degree of polymerisation 198—218, reconverted by 0.5N-NaOMe-MeOH- $\text{N}_2$  into a product having a degree of polymerisation 197. Nitration gives a highly degraded nitrate.  $K_m$  of (IV) and (V) is 0.24—0.32, that of (VI) is  $0.87-1.04 \times 10^{-4}$ . (IV) etc. are thus highly branched compounds. Fractional pptn. from 0.1N- $\text{CaCl}_2$  by MeOH gives fractions having degrees of polymerisation falling from 267 to 182; the derived acetates vary similarly. (IV) is thus not a homogeneous material. The results as a whole show that wood polyoses are of such low degrees of polymerisation that they must be removed from cellulose prior to prep. of fibres or films. R. S. C.

### III.—HOMOCYCLIC.

**Hydrogen fluoride as a condensing agent. XVII. Addition of an alkyl chloride to the ethylenic linking.** J. H. Simons and A. C. Meunier (*J. Amer. Chem. Soc.*, 1943, **65**, 1269—1271; cf. A., 1942, II, 344).—Adding cyclohexene (I) (1 mol.) to  $\text{Bu}^\gamma\text{Cl}$  (1—2 mols.) in HF (2—6 mols.) at  $0-5^\circ$  and keeping at room temp. gives cyclohexyl chloride (II) (65%) and fluoride (11.5%), 3-tert.-butylcyclohexyl chloride (III) (11.1%), b.p.  $98^\circ/20$  mm., aliphatic chlorides, and olefines. The structure of (III) is proved by conversion by boiling KOH-EtOH into an unsaturated hydrocarbon,  $\text{C}_{10}\text{H}_{18}$  (36%), b.p.  $60^\circ/15$  mm., which with aq.  $\text{KMnO}_4$  at  $0^\circ$ —room temp. gives  $\text{CO}_2\text{H}[\text{CH}_2]_3\text{CHMeCO}_2\text{H}$ , m.p.  $114^\circ$  (dianilide, m.p.  $206^\circ$ ), also obtained from 4-tert.-butylcyclohexanol (IV). Further, the Grignard reagent from (III) with  $\text{O}_2$  and then  $\text{NH}_4\text{Cl}$ -ice gives 3-tert.-butylcyclohexanol, b.p.  $119-129^\circ/29$  mm. (3:5-dinitrobenzoate, m.p.  $144^\circ$ ). The 3:5-dinitrobenzoate of (IV) has m.p.  $157.5^\circ$ .  $\text{Bu}^\gamma\text{Cl}$  and  $\text{CMe}_2\text{CHMe}$  in HF give an inseparable mixture.  $\text{Pr}^\beta\text{Cl}$  and (I) give much (II) and a considerable residue, but no aliphatic fraction. R. S. C.

**Derivatives of 1:2:4:5-tetrachlorobenzene. II. N-Nitro-amino-compounds.** A. T. Peters, F. M. Rowe, and D. M. Stead (*J.C.S.*, 1943, 372—373).—2:3:5:6:1- $\text{C}_6\text{HCl}_4\text{NHAc}$  (I) with  $\text{Ac}_2\text{O}-\text{HNO}_3$  ( $d$  1.5) (warmed gradually to  $50^\circ$ ) gives 2:3:5:6-tetrachloro-N-nitroacetanilide (II), m.p.  $131^\circ$  (vigorous decomp.). In boiling xylene, (II) gives (I), 1:2:4:5- $\text{C}_6\text{H}_2\text{Cl}_4$  (III), and a little chloranil (IV) but in boiling PhMe affords (III), (IV), and  $\text{C}_6\text{HCl}_5$ . With boiling aq. AcOH-HCl or -HBr, (II) gives  $\text{C}_6\text{Cl}_6$  or 2:3:5:6:1:4- $\text{C}_6\text{Cl}_6\text{Br}_2$ , respectively, and forms 2:3:5:6:1- $\text{C}_6\text{HCl}_4\text{NH}_2$  (V) with aq. HI-AcOH. 3% aq. NaOH and (II) afford 2:3:5:6-tetrachloro-N-nitroaniline (VI), m.p.  $145-146^\circ$  (vigorous decomp.), also obtained with 4:2:3:5:6:1- $\text{NO}_2\text{C}_6\text{Cl}_4\text{NH}_2$  (VII) from (V) and AcOH- $\text{HNO}_3$  ( $d$  1.5) at  $60^\circ$ . In AcCl, (VI) gives  $\text{C}_6\text{Cl}_6$ , and  $\text{C}_6\text{HCl}_5$ , in AcOH affords (VII), and in AcOH-HHal behaves as (II). Excess of  $\text{HNO}_3$  ( $d$  1.5) in AcOH at  $50^\circ$  converts (V) into 2:3:5:6-tetrachloro-4-nitro-N-nitroaniline (VIII), m.p.  $88-95^\circ$  (according to rate of heating). With  $\text{Me}_2\text{SO}_4$ -10% aq. NaOH, 2:3:5:6-tetrachloro-N-nitromethylaniline, m.p.  $138-139^\circ$ , and its 4- $\text{NO}_2$ -derivative, m.p.  $171-175^\circ$  (decomp.), are obtained from (VI) and (VIII), respectively.  $\text{HNO}_2$  partly converts (VI) and (VIII) into diazonium salts (coupling with 2:3-OH- $\text{C}_{10}\text{H}_6\text{CO}\cdot\text{NHPh}$ ). F. R. S.

**Influence of the 6-nitro-group on the halogenation, nitration, mercuration, and diazo-coupling of 6-nitro-1-naphthylamine and related naphthalides.** H. H. Hodgson and H. S. Turner (*J.C.S.*, 1943, 391—394).—6:1- $\text{NO}_2\text{C}_{10}\text{H}_8\text{NH}_2$  (I) [picrate, m.p.  $197^\circ$ ; formyl, m.p.  $193^\circ$ , mono- (II), m.p.  $205.5^\circ$ , and di-*p*-toluenesulphonyl derivative, m.p.  $204.5-205.5^\circ$ ; 6-nitronaphthyl-1-maleamic acid, m.p.  $181^\circ$ ] gives (Sandmeyer) 1-chloro-, m.p.  $118-120^\circ$ , 1-bromo-, m.p.  $130.5-131^\circ$ , and 1-iodo-6-nitronaphthalene, m.p.  $73^\circ$ .  $\text{Cl}_2$  and 6:1- $\text{NO}_2\text{C}_{10}\text{H}_8\text{NHAc}$  (III) in AcOH at  $90^\circ$  afford the Ac derivative, m.p.  $243^\circ$  (hydrolysed by  $\text{H}_2\text{SO}_4$ -aq. EtOH), of 2:4-dichloro-6-nitro-1-naphthylamine, m.p.  $177-178^\circ$ , whilst Br- $\text{CHCl}_3$  and (I) at  $-5^\circ$  give 4-bromo-6-nitro-1-naphthylamine (IV), m.p.  $123-124^\circ$ , converted (diazo-methods) into 1-bromo-7-nitro-, m.p.  $104-105^\circ$ , and 1:4-dibromo-6-nitro-naphthalene, m.p.  $110^\circ$ . 6-Nitro-1-naphthaleneazo- $\beta$ -naphthol has m.p.  $220^\circ$ . 1:2- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me-p}$  and  $\text{HNO}_3$  ( $d$  1.5) in AcOH at  $30-40^\circ$  (later  $50-60^\circ$ ) give 1-bromo-6-nitro-*p*-toluenesulphon-2-naphthalide, m.p.  $197-198^\circ$ ; the free base affords (Sandmeyer) 1:2-dibromo-6-nitronaphthalene, m.p.  $175^\circ$ , and (diazo-method) 1:6- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NO}_2$ .

Further bromination [as for (I)] of (IV) yields 2:4-dibromo-6-nitro-1-naphthylamine, m.p.  $195^\circ$ . Nitration of (III) followed by hydrolysis gives mainly 4:6-, m.p.  $178^\circ$ , and some 2:6-dinitro-1-naphthylamine, m.p.  $226.5-228.5^\circ$ . (II) with  $\text{HNO}_3$  ( $d$  1.5)-AcOH at  $90^\circ$  affords the *p*-toluenesulphonyl derivative, m.p.  $172.5^\circ$  (hydrolysed by  $\text{H}_2\text{SO}_4$ ) of 2:4:6-trinitro-1-naphthylamine, m.p.  $301-304^\circ$  (decomp.). (I) and  $\text{Hg}(\text{OAc})_2$  in AcOH give the 4-OAc-Hg-derivative, m.p.  $>400^\circ$ , which with KI-I forms 4-iodo-6-nitro-1-naphthylamine, m.p.  $175^\circ$ , converted into 1-bromo-4-iodo-6-nitronaphthalene, m.p.  $130.5-131.5^\circ$ . 6:1:2- $\text{NO}_2\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NH}_2$  gives 1-bromo-2-iodo-6-nitronaphthalene, m.p.  $193-194^\circ$ . *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\text{Cl}$  with (I) affords 6-nitro-4-*p*-toluenazo-1-naphthylamine, m.p.  $242.5^\circ$  (Ac derivative, m.p.  $300-301^\circ$ ), which yields 6-nitro-4-*p*-toluenazo-1-naphthalene-azoresorcinol, m.p.  $>400^\circ$ . Hence the 6- $\text{NO}_2$  group favours reaction at the 4-position. M.p. are corr. F. R. S.

**Preparation of dithizone (diphenylthiocarbazone).** J. H. Billman and (Miss) E. S. Cleland (*J. Amer. Chem. Soc.*, 1943, **65**, 1300—1301).—Adding  $\text{CS}_2$  to  $\text{NHPh}\cdot\text{NH}_2$  in cold  $\text{Et}_2\text{O}$  gives  $\text{NHPh}\cdot\text{NH}\cdot\text{CS}\cdot\text{S}\cdot\text{NH}_2\cdot\text{NHPh}$  (97%), converted at  $96-98^\circ$  (not  $>98^\circ$ ) (bath) into  $\text{H}_2\text{S}$  and  $\text{CS}(\text{NH}\cdot\text{NHPh})$  (60—75%), which in boiling KOH-MeOH gives  $\text{NHPh}\cdot\text{NH}\cdot\text{CS}\cdot\text{N}\cdot\text{NPh}$  (52—66% overall),  $\text{NHPh}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , and  $\text{NH}_2\text{Ph}$ . R. S. C.

**Decomposition of diazo-compounds in neutral solution. The diazo-coupling reaction.** H. H. Hodgson and E. Marsden (*J.C.S.*, 1943, 379—380).—Aq. solutions of diazotised  $\text{NH}_2\text{Ar}$ , when maintained neutral by  $\text{CaCO}_3$ , decompose to form bis- ( $\text{NH}_2\text{Ph}$ , *o*-toluidine) or mono-arylazophenols (*p*-toluidine, *o*-, *m*-, and *p*- $\text{NO}_2\text{C}_6\text{H}_4\cdot\text{NH}_2$ ,  $\alpha$ - and  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ ). An aq. solution of the

equilibrium mixture  $\text{NPh}\cdot\text{N}\cdot\text{OH}$  (I)  $\rightleftharpoons \text{NPh}\cdot\text{N}^+\cdot\text{OH}^-$  (II) decomposes to form nearly equal parts of 2:4-bisbenzeneazo- and 4-benzeneazophenol. The results are held to indicate that undissociated (I) and not (II) is the coupling component. 3-Nitro-4-*m*-, m.p.  $202^\circ$ , and 4-nitro-2-*p*-nitrobenzeneazophenol, m.p.  $168^\circ$ , are described. F. R. S.

**Recovery of phenols and olefines from alkylated phenols.**—See B., 1943, II, 309.

**Ambrettolide and isomerides.** III.—See A., 1943, II, 318.

**Dihydroresorcinols.**—See A., 1943, II, 338.

**Mechanism of fission of ethers. I. Fission of aromatic ethers in non-aqueous solvents.** S. P. Walvekar, N. L. Phalnikar, and B. V. Bhide (*J. Indian Chem. Soc.*, 1943, **20**, 131—136).—Fission of  $\text{PhOMe}$ , *p*- $\text{C}_6\text{H}_4\text{R}\cdot\text{OMe}$  ( $\text{R} = \text{Cl}, \text{Br}, \text{Me}, \text{NO}_2$ ), and *o*- $\text{NO}_2\text{C}_6\text{H}_4\cdot\text{OMe}$  by anhyd. HCl and HBr has been studied. In  $\text{CCl}_4$  or *n*- $\text{C}_6\text{H}_{14}$  ( $\text{PhOMe}$  only) after 50 hr. at  $70^\circ$  or 5 months at room temp. fission is usually  $<1\%$ . With *m*-HBr in  $\text{CCl}_4$  at  $70^\circ$ , addition of 5% of  $\text{C}_5\text{H}_5\text{N}$  produces 1.5—37% fission, 5% of AcOH 2.0—9.3%, of  $\text{NH}_2\text{Ph}$  65% ( $\text{PhOMe}$ ) or 79% (anisidine), and of  $\text{NPhMe}_2$  78% ( $\text{PhOMe}$ ). HBr produces considerable fission in  $\text{PhNO}_2$ ,  $\text{CHCl}_3$ , or AcOH alone; addition of  $\text{C}_5\text{H}_5\text{N}$  increases the amount. A mechanism for the fission is suggested. A. Li.

**Derivatives of creosol.** J. H. Fletcher and D. S. Tarbell (*J. Amer. Chem. Soc.*, 1943, **65**, 1431—1432).—Martin-Clemmensen reduction of vanillin gives creosol (63%), b.p.  $105-106^\circ/15$  mm., the allyl ether (prep. by  $\text{CH}_2\text{CH}\cdot\text{CH}_2\text{Br}$  and NaOH in aq.  $\text{COMe}_2$ ; 86%), b.p.  $128-130^\circ/15$  mm., of which with aq.  $\text{KMnO}_4\text{-Na}_2\text{CO}_3$  gives 3-methoxy-*p*-tolylloxyacetic acid (31%), m.p.  $115-116^\circ$ , or at  $210^\circ$  alone gives 5:1:3:4- $\text{CH}_2\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Me}(\text{OMe})\cdot\text{OH}$  (I) (84%), b.p.  $135-138^\circ/18$  mm. ( $\alpha$ -naphthylurethane, m.p.  $132-132.5^\circ$ ). With  $\text{Me}_2\text{SO}_4$ -2N-NaOH, (I) gives 3:4:1:5- $(\text{OMe})_2\text{C}_6\text{H}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$  (II) (86%), b.p.  $125-135^\circ/12$  mm., oxidised ( $\text{KMnO}_4$ ) to 4:5-dimethoxy-*m*-toluic acid, m.p.  $91.5-92.5^\circ$ , which is also obtained from 3:4:1:5- $(\text{OMe})_2\text{C}_6\text{H}_2\text{Me}\cdot\text{CH}\cdot\text{CHMe}$  (III). KOH in  $\text{O}[(\text{CH}_2)_2\text{OH}]_2$  at  $150-170^\circ$  isomerises (I) to 5-propenylcreosol [3-methoxy-5-propenyl-*p*-cresol], m.p.  $61-62^\circ$ ; at  $175-185^\circ$  (II) similarly gives (III) (39%), b.p.  $109-111^\circ/1$  mm.

**Synthetic oestrogens of the diphenylethane series.** H. Bretschneider, A. de Jonge-Bretschneider, and N. Ajtai (*Ber.*, 1941, **74**, [B], 571—588).—*p*-Hydroxypropiophenoneazine (I), m.p.  $170-171^\circ$  (slight previous sintering), distils unchanged at  $\sim 250^\circ$  (bath)/high vac., is reduced ( $\text{H}_2$ , Pd-C, EtOH) to the hydrazine, which is oxidised directly (I-KOAc) to a  $\text{H}_2$ -derivative (II), decomp.  $\sim 133-150^\circ$  (sinters  $126^\circ$ ), of (I). Oxidation by  $\text{O}_2$  in presence of  $\text{CuSO}_4$  and NaOH gives a resin, decomposed at  $120-150^\circ/1$  mm. to a mixture of *dl*- (III), m.p.  $126-128^\circ$ , and *meso*- (IV), m.p.  $185-187^\circ$ , - $(\text{p-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHEt})_2$ . (II) is methylated ( $\text{Me}_2\text{SO}_4$ ) to the dihydro-*p*-methoxypropiophenoneazine (V), m.p.  $76-78^\circ$  (Földi *et al.*, below), is hydrolysed (MeOH-conc. HCl) to (probably) an anol polymeride, and decomposed at  $140-160^\circ$  to (IV) (62%). *p*-Acetoxypropiophenoneazine, m.p.  $135.5-136.5^\circ$  [from (I) and  $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ ], is similarly reduced and oxidised ( $\text{O}_2\text{-CuSO}_4$ ) to a  $\text{H}_2$ -derivative, m.p.  $115-116^\circ$  [at  $125-150^\circ$  gives *meso*-(*p*-OAc- $\text{C}_6\text{H}_4\cdot\text{CHEt}$ ), m.p.  $140-141^\circ$  (VI)], and oil [gives (VI) also]. (*p*-OMe- $\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}$ ), and  $\text{MgEtBr}$  afford a product [from which (V) is isolable] which at  $130-150^\circ$  (bath)/high vac. yields *dl*- (VII), m.p.  $55^\circ$ , and *meso*- (VIII).

m.p. 144°,  $-(p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHEt})_2$  (cf. Campbell *et al.*, A., 1940, II, 79). (VII) and (VIII) are unaffected by Pd-black at 250° whereas (IV) undergoes fission. With Pd-C at 300° in  $\text{CO}_2$  (VII) yields (VIII) (42%) [and 33% of unchanged (VII)]; (VIII) similarly gives much oil, (?) a little (VII), and 28% of unchanged (VIII). Partial methylation ( $\text{Me}_2\text{SO}_4$  in cold  $\text{MeOH-N-NaOH}$ ) of (IV) affords the  $\text{Me}_2$  ether, m.p. 120—121° (propionate, m.p. 85—87°), also obtained [with (IV)] from (VIII) and aq.  $\text{MeOH-NaOH}$  at 250°, and by thermal decomp. of a mixture of (II) and (V) (m.p. 58—67°). 4-Hydroxy-2-methylacetophenoneazine, m.p. 251—253° (block) (diacetate, m.p. 129—130°, sinters 128°), is reduced ( $\text{H}_2$ , Pd-C, EtOH-AcOH; not EtOH alone), the mixture treated with  $\text{KHCO}_3$ , then oxidised ( $\text{O}_2$ - $\text{CuSO}_4$ ), and the resulting oil heated at 140°; 4:4'-dihydroxy-2:2'-dimethyl- $\beta$ - $\gamma$ -diphenylbutane (IX), m.p. 191—192° [diacetate, m.p. 164°, sinters 161°; dipropionate, m.p. 123—124°;  $\text{Me}_2$  ether (X), m.p. 141—142°], is thereby obtained in poor yield. (X) is similarly prepared starting from 4-methoxy-2-methylacetophenoneazine, m.p. 110—111°, sinters 109° ( $\text{H}_2$ -derivative, m.p. 112—113°, sinters 111°), in 38% yield and is demethylated to (IX). The difference in biological activity of (IV) and diethylstilboestrol is shown by using mice (not rats) in the Allen-Doisy test; (IX) has a high activity. H. B.

**Synthetic oestrogens of the diphenylethane series.** Z. Földi and G. von Fodor (*Ber.*, 1941, 74, [B], 589—595).—*p*-Methoxypropionophenoneazine (I), m.p. 134°, absorbs 2  $\text{H}_2$  on catalytic reduction (Pd-C, 96% EtOH, room temp.) but evaporation of the resulting solution gives an oil (A) and a  $\text{H}_2$ -derivative (II), m.p. 75—77°, of (I). (A) and (II) show the same behaviour on thermal decomp. Reduction of (I) and subsequent atm. oxidation of the product affords (II) and an isomeride (III), m.p. 58—65°, which undergo thermal decomp. to a mixture of *meso*-, m.p. 144°, and *dl*-( $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHEt})_2$ , m.p. 55° [demethylated by  $\text{MeOH-KOH}$  at 200° or  $\text{AcOH-HBr}$  to *meso*- and *dl*-( $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHEt})_2$ , respectively]. (II) and (III) may be stereoisomeric forms of ( $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHEt}\cdot\text{N}$ ) $_2$ . H. B.

**Preparation of the oestrogen  $\beta$ -bromo- $\beta$ -phenyl- $\alpha\alpha$ -di-*p*-phenylethylene.** W. Tadros and A. Schönberg (*J.C.S.*, 1943, 394).—( $p\text{-OEt}\cdot\text{C}_6\text{H}_4$ ) $_2\text{CO}$  and  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  give  $\beta$ -phenyl- $\alpha\alpha$ -di-*p*-phenylethyl alcohol, m.p. 124°, which on distillation with a little 20%  $\text{H}_2\text{SO}_4$  in a vac. yields  $\beta$ -phenyl- $\alpha\alpha$ -di-*p*-phenylethylene, m.p. 74°, brominated ( $\text{Br-AcOH}$ ) to the  $\beta$ -Br-compound, m.p. 97—98°. F. R. S.

**Rapid and practical method of preparation of 4-amino-2-methyl-1-naphthol hydrochloride (vitamin- $\text{K}_2$ ) from 2-methyl-1:4-naphthoquinone.** P. P. T. Sah and W. Brüll (*Ber.*, 1941, 74, [B], 552—554).—1:2:4- $\text{O}\cdot\text{C}_{10}\text{H}_7\text{Me}\cdot\text{N}\cdot\text{OH}$  (from the quinone and  $\text{NH}_2\text{OH}\cdot\text{AcOH}$  in EtOH) is treated with aq.  $\text{NaOH}$  and the resulting 4:2:1- $\text{NO}\cdot\text{C}_{10}\text{H}_5\text{Me}\cdot\text{ONa}$  reduced ( $\text{Sn}$ , aq.  $\text{HCl}$ ) to 1:2:4- $\text{OH}\cdot\text{C}_{10}\text{H}_5\text{Me}\cdot\text{NH}_2\cdot\text{HCl}$ , m.p. 280° (decomp.) (darkens  $\sim 262^\circ$ ). H. B.

**Stereoisomeric forms of additive compounds of alcohols and substituted 7-nitrostilbenes.** B. Reichert and W. Kuhn (*Ber.*, 1941, 74, [B], 328—337).—(*trans*)-7-Nitro-4'-methoxystilbene [ $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CPh}\cdot\text{NO}_2$ ] (I) and  $\text{MeOH-KOH}$  give (cf. Meisenheimer *et al.*, A., 1907, i, 858), in addition to the known ( $\alpha$ -) form, m.p. 139° (up to 80%), of  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})\cdot\text{CHPh}\cdot\text{NO}_2$ , a  $\beta$ -form, m.p. 77° (10—35%; amount increases with rise in temp. of reaction mixture), and some *cis*-(I), m.p. 112—113° (cf. Flürscheim *et al.*, A., 1932, 730). *trans*-7-Nitro-3':4'-methylenedioxy stilbene (II), m.p. 129—129.5° (corr.), similarly affords  $\alpha$ -, m.p. 149—150°, and  $\beta$ -forms, m.p. 128—129°, of  $\alpha$ -nitro- $\beta$ -methoxy- $\alpha$ -phenyl- $\beta$ -3:4-methylenedioxyphenylethane, a little of the *cis*-form (III), m.p. 123—123.5° (corr.), of (II), and some 3:5-diphenyl-4-3':4'-methylenedioxyphenylisooxazole. 7-Nitro-3':4':5'-trimethoxystilbene and cold  $\text{MeOH-KOH}$  give 83% of the  $\alpha$ -, m.p. 142—143°, and traces of the  $\beta$ -form (IV), m.p. 138—139°, of  $\alpha$ -nitro- $\beta$ -methoxy- $\alpha$ -phenyl- $\beta$ -3:4:5-trimethoxyphenylethane; at the b.p. (IV) and 3:5-diphenyl-4-3':4':5'-trimethoxyphenylisooxazole, m.p. 162—163°, result. *trans*-7-Nitro-3':4'-dimethoxystilbene (V), m.p. 109°, similarly gives one form only of  $\alpha$ -nitro- $\beta$ -methoxy- $\alpha$ -phenyl- $\beta$ -3:4-dimethoxyphenylethane, m.p. 120—121°; (VI) (below) and 3:5-diphenyl-4-3':4'-dimethoxyphenylisooxazole, m.p. 170—171°, are by-products. Ultra-violet irradiation of (II) and (V) in  $\text{MeOH}$  gives (III) and *cis*-7-nitro-3':4'-dimethoxystilbene (VI), m.p. 102—103° (corr.), respectively. 7-Nitro-4'-methoxy-3'-chloromethylstilbene, m.p. 108—109° [from 4:3:1- $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{CH}_2\text{Cl})\cdot\text{CHO}$  and  $\text{CH}_2\text{Ph}\cdot\text{NO}_2$  in EtOH- $\text{NH}_2\text{Me}$ ], and  $\alpha$ -nitro- $\alpha$ -phenyl- $\beta$ -2-furylethylene (VII) do not add  $\text{MeOH}$ . (VII) is reduced ( $\text{H}_2$ , Pd-C,  $\text{C}_5\text{H}_5\text{N}$ , room temp.) to *Ph furfuryl ketoxime*, m.p. 90°, further reduced ( $\text{Na-Hg}$ , 50%  $\text{AcOH}$ ) to  $\alpha$ -phenyl- $\beta$ -2-furylethylamine, b.p. 158—160°/30 mm. [hydrochloride, m.p. 206—208° (decomp.)]. The above  $\alpha$ - and  $\beta$ -forms are racemates. H. B.

**Thermal decomposition of polyarylated carbinols.** C. F. H. Allen and J. A. VanAllan (*J. Amer. Chem. Soc.*, 1943, 65, 1384—1389).—2:3:4:5-Tetraphenylcyclopentadienone (I) and  $\text{MgPhBr}$  in  $\text{Et}_2\text{O}$  or  $\text{C}_6\text{H}_6$  give, by 1:2-addition, 1:2:3:4:5-pentaphenyl- $\Delta^{2:4}$ -cyclopentadienol (II) (Ziegler *et al.*, A., 1926, 57), but in boiling (*iso*- $\text{C}_5\text{H}_{11}$ ) $_2\text{O}$  give, by 1:4-addition, 2:3:3:4:5-pentaphenyl- $\Delta^{1:4}$ -cyclopentadienol (III), m.p. 189° (1 active H; no addition of  $\text{MgMeI}$ ).

Formation of (III) is direct, since the  $\text{Mg}$  derivative of (II) is unchanged in boiling (*iso*- $\text{C}_5\text{H}_{11}$ ) $_2\text{O}$ . Distilling or heating (II) at 290—300° gives (III) and 2:3:3:4:5-pentaphenyl- $\Delta^4$ -cyclopentenone (IV), m.p. 164° (adds 1  $\text{MgMeI}$ ; no active H), with small amounts of 1:2:3:4:5-pentaphenylcyclopentadiene, m.p. 250°,  $\text{H}_2\text{O}$ , and  $\text{PhCHO}$ ; the main reaction is thus an allylic shift of  $\text{Ph}$ . (III) is converted into (IV) by boiling 48%  $\text{HBr-AcOH}$ , and (IV) into (III) by  $\text{NaNH}_2$  in boiling xylene.  $\text{CrO}_3\text{-Ac}_2\text{O}$  oxidises (III) or (IV) to  $\text{BzOH}$  and  $\text{COPh}_2$  as sole products. ( $\text{CH}\cdot\text{CO}$ ) $_2\text{O}$  and (II) at the m.p. give 3:4:5:6-tetraphenyl-3:6-endo- $\alpha$ -hydroxybenzylidene- $\Delta^4$ -tetrahydrophthalic anhydride, m.p. 220°, which, when distilled, regenerates (II) and so yields (III) and (IV).  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$  and (I) in  $\text{C}_6\text{H}_6$  give 2:3:4:5-tetraphenyl-1-*p*-anisylcyclopentadienol, m.p. 203°; 1:4-addition could not be effected. The presence of  $\text{CH}\cdot\text{CO}$  in (IV) is proved by conversion by  $\text{MgPhBr}$  into 1:2:3:4:4:5-hexaphenyl- $\Delta^2$ -cyclopentenol, m.p. 248° (1 active H; does not add  $\text{MgMeI}$ ), dehydrated by  $\text{Ac}_2\text{O}$  or  $\text{AcCl}$  to 1:2:3:4:5:5-hexaphenyl- $\Delta^{1:3}$ -cyclopentadiene, m.p. 172°;  $\text{MgMeI}$  gives by addition and simultaneous dehydration 1:3:4:5:5-pentaphenyl-1-methyl- $\Delta^{1:3}$ -cyclopentadiene (? 1:2:3:3:4-pentaphenyl-5-methylene- $\Delta^1$ -cyclopentene), m.p. 159°. 2:3:4:5-Tetraphenyl- $\Delta^2$ -cyclopentenone (V) and  $\text{MgMeI}$  give 1:2:4:5-tetraphenyl-3-methyl- $\Delta^{1:3}$ -cyclopentadiene (or 1:2:4:5-tetraphenyl-3-methylene- $\Delta^1$ -cyclopentene), m.p. 163°.  $\text{C}_6\text{H}_5\text{-AlCl}_3$  does not affect (IV) or (V), but converts (I) or the bimol. product from  $\alpha\beta$ -dimethylanhydroacetonebenzil, by reduction, into 2:3:4:5-tetraphenyl- (VI), m.p. 328°, and diphenyldimethyl-cyclopentanone, respectively.  $\text{MgPhBr}$  and (VI) give 1:2:3:4:5-pentaphenylcyclopentanone, m.p. 254°. Attempts to prepare (IV) from  $\text{CO}(\text{CH}_2\text{Ph})_2$  or  $\text{OH}\cdot\text{CPh}_2\cdot\text{COPh}$  failed. At 290—300° 2:3:4:5-tetraphenyl-1-benzyl- $\Delta^{2:4}$ -cyclopentadienol (VII) gives 1:2:3:4-tetraphenyl-5-benzylidene- $\Delta^{1:3}$ -cyclopentadiene (47%) with smaller amounts of ( $\text{CHPh}$ ) $_2$ , (by the alternative mode of decomp.) (I) +  $\text{PhMe}$ , and a substance (VIII) (1%), m.p. 158°. Styrene and (I) in warm  $\text{C}_6\text{H}_6$  give 3:6-endo-1:2:3:4:6-pentaphenyl- $\Delta^1$ -cyclohexene [1:2:4:5:6-pentaphenyl-[2:2:1]-dicyclo- $\Delta^5$ -hepten-7-one] (IX), m.p. 191° (adds 1  $\text{MgMeI}$ ; no active H), converted by  $\text{MgPhBr}$  into 1:2:3:4:6-pentaphenyl-3:6-endo- $\alpha$ -hydroxybenzylidene- $\Delta^1$ -cyclohexene (89%), m.p. 258°, which, when heated, gives (IV), a compound (X),  $\text{C}_{36}\text{H}_{28}\text{O}$ , m.p. 172°, and small amounts of styrene and  $\text{PhCHO}$ . With  $\text{CH}_2\text{Ph}\cdot\text{MgBr}$  in  $\text{C}_6\text{H}_6$  or  $\text{MgMeI}$  in (*iso*- $\text{C}_5\text{H}_{11}$ ) $_2\text{O}$ , (IX) gives 1:2:3:4:6-pentaphenyl-3:6-endo- $\alpha$ -hydroxy- $\beta$ -phenylethylidene- (XI), m.p. 212°, or - $\alpha$ -hydroxyethylidene-, m.p. 209° (1 active H; does not add  $\text{MgMeI}$ ), - $\Delta^1$ -cyclohexene, respectively, but it does not react with 1- $\text{C}_{10}\text{H}_7\cdot\text{MgBr}$ .  $\text{MgMeI}$  or  $\text{Ac}_2\text{O}$  does not affect (X), but 72%  $\text{HClO}_4\text{-Ac}_2\text{O}$  (not  $\text{HBr}$  or  $\text{HI}$ ) at the b.p. gives  $\text{C}_6\text{HPh}_5$ . In boiling  $\text{C}_6\text{H}_6$ , ( $\text{C}\cdot\text{CO}_2\text{Me}$ ) $_2$  and (II) give  $\text{Me}_2$  3:4:5:6-tetraphenyl-3:6-endo- $\alpha$ -hydroxybenzylidene-3:6-dihydrophthalate, m.p. 209°, which at 250° gives 3:4:5:6:1:2- $\text{C}_6\text{Ph}_4(\text{CO}_2\text{Me})_2$  (75%) and  $\text{PhCHO}$ .  $\text{Ac}_2\text{O}$  or  $\text{AcCl}$  does not dehydrate (VII) but yields the acetate, m.p. 195°; (II) similarly yields its acetate, m.p. 158° [not (VIII)], converted by  $\text{HCl-AcOH}$  into the known 1-chloro-1:2:3:4:5-pentaphenyl- $\Delta^{2:4}$ -cyclopentadiene. The decomp. of the bridged-ring compounds by heat occurs at the linking  $\text{C}\cdot\text{C}\cdot\text{C}$ . R. S. C.

**Hydrogenolysis of sulphur compounds by Raney nickel catalyst.**—See A., 1943, II, 293.

**Multiplication process for the separation of racemates.**—See A., 1943, I, 275.

**Synthesis of pharmacologically important carboxylic acids. III. Control of hydrogenation of *O*-acetylmandelic acid esters.** K. Kindler. **IV. Synthesis of substituted  $\beta$ -phenylpropionic acids from aryl ethyl ketones.** K. Kindler and T. Li (*Ber.*, 1941, 74, [B], 315—321, 321—327; cf. A., 1936, 1508).—III.  $\text{OAc}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$  (I) is unaffected by  $\text{H}_2$  (2.5 atm.)-Pd-black in  $\text{AcOH}$  at room temp. but at 100° 4  $\text{H}_2$  are rapidly consumed and Et cyclohexylacetate (II) results. Interruption of the reaction after absorption of 1  $\text{H}_2$  gives (I),  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$  (65%), and a little (II); the 3:4-( $\text{OMe}$ ) $_2$ - and - $\text{CH}_2\text{O}_2$ -derivatives of (I) similarly give  $\text{CH}_2\text{Ar}\cdot\text{CO}_2\text{Et}$  although the use of a highly active catalyst leads to some nuclear hydrogenation. Suppression of nuclear hydrogenation is, however, effected by addition of  $\text{HZnCl}_3$  or, better,  $\text{HBr}$ . Thus  $\text{OAc}\cdot\text{CHAr}\cdot\text{CO}_2\text{Me}$  (A) with  $\text{H}_2$ -Pd-black in  $\text{AcOH-H}_2\text{SO}_4\text{-HBr}$  or  $\text{AcOH-HBr}$  at room temp. give 84—95% of  $\text{CH}_2\text{Ar}\cdot\text{CO}_2\text{Me}$  [ $\text{Ar} = p\text{-anisyl}$ , b.p. 158°/19 mm., 3:4-( $\text{OMe}$ ) $_2\text{C}_6\text{H}_3$ , b.p. 175°/15 mm., 3:4-( $\text{OEt}$ ) $_2\text{C}_6\text{H}_3$ , b.p. 180—181°/18 mm., 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$ , b.p. 170—171°/16 mm. (free acids, m.p. 86°, 99—100°, 79—80°, and 128°, respectively)].  $p\text{-C}_6\text{H}_4\text{R}\cdot\text{CH}(\text{OAc})\cdot\text{CO}_2\text{Et}$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{Ph}$ , cyclohexyl) are rapidly reduced in  $\text{AcOH-HClO}_4$  (or - $\text{H}_2\text{SO}_4$ ) at room temp. to  $p\text{-C}_6\text{H}_4\text{R}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ ; reaction does not occur in presence of  $\text{HBr}$ . The following are prepared (75—85% yield) from  $\text{OAc}\cdot\text{CHAr}\cdot\text{CN}$  and  $\text{HCl}$  in  $\text{MeOH}$  or  $\text{EtOH}$  containing a little  $\text{H}_2\text{O}$ : (A),  $\text{Ar} = p\text{-anisyl}$ , b.p. 166—167°/14 mm., 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$ , b.p. 181°/14 mm., 3:4-( $\text{OMe}$ ) $_2\text{C}_6\text{H}_3$ , b.p. 195°/16 mm., and 3:4-( $\text{OEt}$ ) $_2\text{C}_6\text{H}_3$ , b.p. 192°/14 mm.;  $\text{OAc}\cdot\text{CHAr}\cdot\text{CO}_2\text{Et}$ ,  $\text{Ar} = \text{Ph}$ , b.p. 160°/28 mm., *p*-tolyl, b.p. 150°/14 mm., m.p. 74°, *p*- $\text{C}_6\text{H}_4\text{Et}$ , b.p. 166°/12 mm., *p*-xenyl, b.p. 227°/14 mm., m.p. 67°, *p*-cyclohexylphenyl, b.p.

211°/11 mm., m.p. 53°, and 3:4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, b.p. 195°/14 mm. IV. COArEt, NHMe<sub>2</sub>, and S at 140—150° give CH<sub>2</sub>Ar·CH<sub>2</sub>·CS·NMe<sub>2</sub> (B) presumably thus: COArEt + NHMe<sub>2</sub> → NMe<sub>2</sub>·CArEt·OH → S·NMe<sub>2</sub>·CArEt·OH → [S·NMe<sub>2</sub>·CAr·CHMe] → (B). The following β-arylthiopropiondimethylamides are described: aryl = *p*-tolyl, b.p. 225°/18 mm., m.p. 48—49°, *p*-C<sub>6</sub>H<sub>4</sub>Et, b.p. 295—310°/13 mm., *p*-C<sub>6</sub>H<sub>4</sub>F, b.p. 220°/26 mm., m.p. 57—58°, *p*-C<sub>6</sub>H<sub>4</sub>Cl, m.p. 64°, *p*-C<sub>6</sub>H<sub>4</sub>Br, b.p. 243°/17 mm., m.p. 71—72°, *p*-C<sub>6</sub>H<sub>4</sub>I, m.p. 112—113°, *p*-anisyl, b.p. 240—250°/17 mm., 3:4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, m.p. 94°, 4:3-OMe·C<sub>6</sub>H<sub>3</sub>Me, m.p. 83°, *p*-SMe·C<sub>6</sub>H<sub>4</sub>, m.p. 67°, and 4:1-OMe·C<sub>10</sub>H<sub>6</sub>, m.p. 160—170°. Hydrolysis (10% KOH) of (B) affords Ar·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H; β-*p*-fluoro-, m.p. 91°, and *p*-methylthiol-phenyl-, m.p. 101°, *p*-6-methoxy-*m*-tolyl-, m.p. 99—100°, and *p*-4-methoxy-1-naphthyl-propionic acid, m.p. 170—171°, are new. *p*-Fluoropropiophenone, b.p. 105—107°/22 mm., and 4-methoxy-1-naphthyl Et ketone, b.p. 205°/15 mm., m.p. 57°, are prepared from PhF and α-C<sub>10</sub>H<sub>7</sub>·OMe with EtCOCl and AlCl<sub>3</sub> in CS<sub>2</sub> at 0°—room temp. and 0°—50—60°, respectively. H. B.

**Iodinated organic compounds as contrast media for radiographic diagnoses.** II. Ethyl esters of iodinated straight- and branched-chain phenyl-fatty acids. J. T. Plati [with W. H. Strain and S. L. Warren] (*J. Amer. Chem. Soc.*, 1943, **65**, 1273—1276; cf. A., 1942, II, 311).—Adding coarsely crushed, cryst. NaNO<sub>2</sub> to Ph·[CH<sub>2</sub>]<sub>n</sub>·CO<sub>2</sub>H and I in 10:1 (vol.) AcOH—H<sub>2</sub>SO<sub>4</sub> and boiling with stirring gives a mixture whence by crystallisation only the *p*-I-acid is isolated; yields are 39—50% for acids with an odd and 14—45% for acids with an even no. of C. NaIO<sub>3</sub>, but not HNO<sub>3</sub>, may replace the NaNO<sub>2</sub>. Thus are obtained *p*-C<sub>6</sub>H<sub>4</sub>I·CH<sub>2</sub>·CO<sub>2</sub>H, β-*p*-iodophenylpropionic, m.p. 139—141° (Et ester, b.p. 140°/2 mm.), γ-*p*-iodophenyl-*n*-butyric, m.p. 89—90·5° (Et ester, b.p. 146—148°/0·8 mm.), δ-*p*-iodophenyl-*n*-valeric (I), m.p. 109·5—110·5° [Et ester (II), b.p. 158°/2 mm.], ε-*p*-iodophenyl-*n*-hexoic, m.p. 66—67° (Et ester, b.p. 158—160°/2 mm.), and ζ-*p*-iodophenyl-*n*-heptoic acid, m.p. 93—94·5° [Et ester (III), b.p. 175—177°/2·5 mm.]. Ph·[CH<sub>2</sub>]<sub>4</sub>·CO<sub>2</sub>H (IV), m.p. 59—60°, is obtained from Ph·[CH<sub>2</sub>]<sub>3</sub>·Br (V) and CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> etc. or in 70% over-all yield by successively condensing CHPh·CH·CHO with COMe<sub>2</sub>—10% NaOH at room temp., oxidising with aq. NaOCl at 40—50°, rising to 60—65°, and hydrogenating in EtOH in presence of Raney Ni at 110°. HNO<sub>3</sub> at >80° (cool to 60°) converts (IV) into δ-*p*-nitro- (28%), m.p. 84—85° (oxidised by aq. CrO<sub>3</sub> at 75—120° to *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H), which with Fe(OH)<sub>2</sub>—aq. NH<sub>3</sub> gives δ-*p*-amino-phenyl-*n*-valeric acid (42%), m.p. 113—113·5°, and thence (Sandmeyer) (I) (oxidised by alkaline KMnO<sub>4</sub> to *p*-C<sub>6</sub>H<sub>4</sub>I·CO<sub>2</sub>H). CHEt(CO<sub>2</sub>Et)<sub>2</sub> with *p*-C<sub>6</sub>H<sub>4</sub>I·CH<sub>2</sub>Br or (V) gives Et<sub>2</sub> *p*-iodobenzyl- (64%), b.p. 176—180°/2 mm., or γ-phenyl-*n*-propyl-ethylmalonate (58%), b.p. 193—196°/11 mm., and thence Et α-*p*-iodobenzyl-*n*-butyrate (52%), b.p. 182—183°/14 mm., or δ-phenyl-α-ethyl-*n*-valeric acid (VI) (80%), b.p. 189—190°/14 mm., respectively. CHBu<sup>a</sup>(CO<sub>2</sub>Et)<sub>2</sub> gives similarly Et<sub>2</sub> *p*-iodobenzyl-*n*-butylmalonate (67%), b.p. 178—182°/2 mm., and thence Et α-*p*-iodobenzyl-*n*-hexoate (68%), b.p. 156°/2 mm. NaNO<sub>2</sub>—I etc. converts (VI) into an oily I-acid [Et ester (61%), b.p. 162—164°/2 mm.]. (II) and (III) are the most suitable X-ray contrast media but are somewhat toxic in the spinal canal. (II) is very suitable in various other body cavities. R. S. C.

**1-Naphthylacetic acid.**—See B., 1943, II, 310.

**Iodination of tyrosine by iodine monochloride.** P. Block, jun., and G. Powell (*J. Amer. Chem. Soc.*, 1943, **65**, 1430—1431).—Tyrosine and ICl in AcOH, later AcOH—H<sub>2</sub>O, at 60° give 85% of the pure I<sub>2</sub>-derivative, m.p. 201° (corr.). R. S. C.

**Thioketonic esters.** X. K. Chandra, N. K. Chakrabarty, and S. K. Mitra (*J. Indian Chem. Soc.*, 1942, **19**, 139—144).—Et thio-cyclo-pentanone- (I), b.p. 110°/5·5 mm. [free acid (II), m.p. 122° (decomp.)], and -hexanone-2-carboxylate (III), b.p. 112°/6 mm. [free acid (IV), m.p. 115° (decomp.)] (from the CO-esters in EtOH with anhyd. HCl followed by H<sub>2</sub>S at 0°), with mol. Na followed by the appropriate halide in C<sub>6</sub>H<sub>6</sub> at 25° yield Et 1-ethyl-, b.p. 115°/6 mm. (free acid, m.p. 177°), and 1-carbethoxymethyl-thiol-Δ<sup>1</sup>-cyclopentene- (V), b.p. 170°/3 mm., and 1-ethyl-, b.p. 125°/3 mm. (free acid, m.p. 146°), and 1-acetyl-thiol-Δ<sup>1</sup>-cyclohexene-2-carboxylate, b.p. 132°/5 mm. With the appropriate aldehyde in saturated EtOH—HCl at 0°, (II) gives benzylidene-, m.p. 221° (decomp.), *p*-anisylidene-, m.p. 185° (decomp.), and cinnamylidene-bis-(2-carboxy-Δ<sup>1</sup>-cyclopentenyl) thioether, m.p. 127°; (I) yields methylene-, m.p. 117°, benzylidene-, m.p. 140°, *p*-anisylidene-, m.p. 118°, and vanillylidene-bis-(2-carbethoxy-Δ<sup>1</sup>-cyclopentenyl) thioether, m.p. 136°; (IV) gives 4-keto-2-phenyl-, m.p. 85° [also obtained from (III) and PhCHO], -2-*p*-anisyl-, m.p. 124°, and -2,4'-hydroxy-3'-methoxyphenyl-5:6-tetramethylene-1:3-thioxine, m.p. 178°. (III) with mol. Na in C<sub>6</sub>H<sub>6</sub> CH<sub>2</sub>—CH—C·OH at room temp., then CH<sub>2</sub>Cl·CO<sub>2</sub>Et at the b.p., yields 2-hydroxy-6-carbethoxy-3:4:5:8-tetrahydrothionaphthen, m.p. 59°. (V) and Na in C<sub>6</sub>H<sub>6</sub> give the ester (A), b.p. 140°/5 mm., m.p. 54°. Iodometric measurements show that in EtOH at 30° and 60° (I) contains 36·6 and 35·1% respectively, while (III) contains 77·4 and 75·7% respectively, of the thiol form. A. L.

**Steric course and mechanism of the diene reaction.** F. Bergmann and H. E. Eschinazi (*J. Amer. Chem. Soc.*, 1943, **65**, 1405—1411).—The main product of a Diels-Alder reaction is sometimes accompanied by a small amount of an isomeride. In both products the configuration of the singly unsaturated reactant is retained. The isomerism is not due to stereoisomerism but to a shift of the newly formed ethylenic linking. This postulates simultaneous reaction of both poles of the reactants, >C<sup>+</sup>·C<sup>+</sup>·C<sup>+</sup>·C<sup>+</sup>·C<sup>+</sup>·C<sup>+</sup> and >C<sup>+</sup>·C<sup>+</sup>·C<sup>+</sup>·C<sup>+</sup>·C<sup>+</sup>·C<sup>+</sup>; in accordance with this view, dienes which contain large amounts of the resonance form illustrated react readily, and olefines must contain "resonance-producing" groups (CO, CN, CO<sub>2</sub>H, etc.). In an open tube di-Δ<sup>1</sup>-cyclohexenyl (I) and CHPh·CH·CO<sub>2</sub>H at 175° or 250° give only 9-phenyl-Δ<sup>12</sup>-dodecahydrophenanthrene-10-carboxylic acid (II), m.p. 231° (A., 1938, II, 330; m.p. 221°), but in a sealed tube give also a small amount of an "ethylenic" isomeride (III), m.p. 282°. With CH<sub>2</sub>N<sub>2</sub>, (II) gives the Me ester (IV), m.p. 111—112°, which is unaffected by NaOH- or NaOEt-EtOH and with NaOBu-BuOH regenerates (II); hydrolysis of the Et ester also gives (II). The Me ester (V), m.p. 147°, of (III) is formed slowly and with NaOBu-BuOH regenerates (III). It follows that (II) and (III) are not stereoisomeric at C<sub>(9)</sub>—C<sub>(10)</sub>. (II) is not decarboxylated by basic Cu carbonate in boiling quinoline or by soda-lime at 350°. CHPh·CH·COMe and (I) at 175° in an open flask or sealed tube give only 10-acetyl-9-phenyl-Δ<sup>12</sup>-dodecahydrophenanthrene (VI) (27%), m.p. 135°, and condensation products of the ketone. (VI) gives no hydrazone or semicarbazone and is unaffected by Al(OPr<sup>i</sup>)<sub>3</sub>-xylene. CHPh·CH·COPh and (I) at 180—185° in an open vessel give 10-benzoyl-9-phenyl-Δ<sup>12</sup>-dodecahydrophenanthrene (VII), m.p. 216° (no CO derivative), and a small amount of an "ethylenic" isomeride (VIII), m.p. 153—154° (no CO derivatives). When *trans*-(CHBz)<sub>2</sub> and (I) are heated for 3 hr. in boiling xylene, 9:10-dibenzoyl-Δ<sup>12</sup>-dodecahydrophenanthrene (IX), dimorphic, (a) yellow, m.p. 182° (stable), and (b) colourless, m.p. 162°, is obtained; these forms are probably not isomerides, since recrystallisation converts (b) into (a); only (a) is obtained if the reactants are heated for 6 hr. in boiling xylene or in PhNO<sub>2</sub> at 150° to the b.p. With a little H<sub>3</sub>PO<sub>4</sub> in boiling Ac<sub>2</sub>O, (IX) gives 2':5'-diphenylfurano-3':4'-9:10-Δ<sup>12</sup>-dodecahydrophenanthrene, fluorescent, m.p. 179—180°, which does not add (·CH·CO)<sub>2</sub>O but in H<sub>2</sub>SO<sub>4</sub> at ~80° gives non-fluorescent (?) 10-phenyl-1:2:3:4-bistetramethylene-1:4-dihydro-9-anthrone, m.p. 141°. *trans*-CHBz·CH·CO<sub>2</sub>H and (I) at 170—180° or in boiling xylene or EtOH give 22—27% of 9-benzoyl-Δ<sup>12</sup>-dodecahydrophenanthrene-10-carboxylic acid (X), m.p. 258—259°, converted by CH<sub>2</sub>N<sub>2</sub> (not HCl-MeOH) into the Me ester, m.p. 159—160°, and by H<sub>2</sub>SO<sub>4</sub> at room temp. into a substance, C<sub>22</sub>H<sub>28</sub>O<sub>4</sub>, m.p. 124—125°; (X) could not be cyclised. None of the adducts reacts with Grignard reagents under normal conditions. MgMeI (not MgPhBr) reacts [no solvent at 100° (bath)] with (IV) [not (V)] to give (VI). With MgMeI in boiling PhMe, (VI) gives 9-phenyl-10-α-hydroxyisopropyl- (60%), b.p. 190—200°/4 mm., but with MgPhBr in boiling xylene (not PhMe) gives (?) 9-phenyl-10-α-phenylethylidene- or -10-α-phenylvinyl- (XI), m.p. 106—107°, -Δ<sup>12</sup>-dodecahydrophenanthrene. MgMeI and (VII) in boiling PhMe give (?) (XI), m.p. 156°, but (VIII) gives only a trace of a yellow oil. R. S. C.

**Friedel-Crafts reactions of 9-phenyldodecahydrophenanthrene-10-carboxylic acid.** H. E. Eschinazi and F. Bergmann (*J. Amer. Chem. Soc.*, 1943, **65**, 1411—1412).—9-Phenyl-Δ<sup>12</sup>-dodecahydrophenanthrene-10-carboxylic acid (I), m.p. 231°, with PCl<sub>5</sub>·C<sub>6</sub>H<sub>6</sub> gives the acid chloride, which with hot NH<sub>2</sub>Ph gives the anilide, m.p. 307—308°, with AlCl<sub>3</sub>·C<sub>6</sub>H<sub>6</sub> at the b.p. gives 10-benzoyl-9-phenyl-Δ<sup>12</sup>-dodecahydrophenanthrene, m.p. 198—199° (at room temp. oils are formed), and with SnCl<sub>4</sub> in boiling light petroleum gives 9-phenyl-1:2:3:4:5:6:7:8-octahydrophenanthrene (II), m.p. 94°, probably by way of 10-chloro-9-phenyl-Δ<sup>12</sup>-dodecahydrophenanthrene. S at 200—260° or Se at 320—340° converts (II) into 9-phenylphenanthrene (III). Se and (I) give 9-phenylphenanthrene-10-carboxylic acid; S affords (III). The isomeride, m.p. 281°, of (I) (preceding abstract) gives an anilide, m.p. 247—248°, but its acid chloride does not react with SnCl<sub>4</sub>. R. S. C.

**Preparation of organic peracids.**—See B., 1943, II, 310.

**Condensations by sodium.** XXVI.—See A., 1943, II, 345.

**Bromine value of aromatic ethylenic ketones.** P. Duquéniois and Z. Sezer (*Rev. Fac. Sci. Istanbul*, 1942, **7**, 98—106).—The Br val. of these ketones determined according to Volmar *et al.* (B., 1928, 326) in the dark is usually in accordance with or slightly > the theoretical val. COMe·CH·CHPh affords the dibromide, m.p. 125° (phenylhydrazone, m.p. 205—206°). COPh·CH·CHPh gives almost exclusively the α-dibromide, m.p. 153—155°. The corresponding tetrabromide, m.p. 208°, is derived from CO(CH·CHPh)<sub>2</sub>. COMe·[CH·CH]<sub>2</sub>·Ph gives a somewhat low Br val. Unstable resinous products are obtained from *o*-OH·C<sub>6</sub>H<sub>4</sub>·CH·CH·COR (R = Me, Ph). Vanillylideneacetone gives a normal Br val. in the dark but results are high in the light. H. W.

**Hydrogen fluoride as a condensing agent.** XVIII. Ar[yl] alkyl ketones. J. H. Simons and E. O. Ramler (*J. Amer. Chem. Soc.*, 1943, **65**, 1390—1392; cf. A., 1942, II, 344).—COPhMe is unchanged in HF at 25°, but at 50° gives dyponone (I) (23·8), BzOH

(16.2), and resin (20%), and at 99° gives BzOH (34) and resin (46%). Similarly, CPhEt in HF at 55° gives BzOH (59), resin (30), and CPhEt·CMe·COPh (3.5%), but at 99° gives only BzOH (34.4) and resin (60%). In HF at 99° (I) gives resin (57) and BzOH (34%), *p*-C<sub>6</sub>H<sub>4</sub>Bu<sup>γ</sup>·CMe gives resin (43) and *p*-C<sub>6</sub>H<sub>4</sub>Bu<sup>γ</sup>·CO<sub>2</sub>H (33%), and CPhBu<sup>β</sup> gives resin (75%) but no acid. HF does not affect CPh<sub>2</sub> at 99° or CPh·CCl<sub>3</sub> at 169°. The resin from CPhMe, when heated to >300°, gives a small amount of an unsaturated liquid, b.p. ~164°, which with cold neutral KMnO<sub>4</sub> gives CPhMe, and thus contains units CPhMe·C. O<sub>2</sub> does not increase the yield of BzOH from CPhMe, nor does addition of CPhMe lead to formation of BzOH from CPh<sub>2</sub>. The reaction mechanism is thus: 2COPh·CH<sub>2</sub>R → COPh·CHR·CPh(CH<sub>2</sub>R)·OH → COPh·CR'·CPh·CH<sub>2</sub>R → CH<sub>2</sub>R·CPh·CHR + BzF (→ BzOH), resin being formed at each stage. The reaction cannot proceed beyond the first stage for COPh·CHRR' and not at all for COPh·CRR'R'' or COPhAr.

R. S. C.

**Photochemical pinacolinisation.** F. Bergmann and Y. Hirshberg (*J. Amer. Chem. Soc.*, 1943, **65**, 1429—1430).—The formation of pinacols by illumination of ketones (A., 1938, II, 348) is influenced by the nature of the aryl nucleus, side-chain, and substituents. No pinacol is formed from 1- or 2-C<sub>10</sub>H<sub>7</sub>·CMe, 1-C<sub>10</sub>H<sub>7</sub>·COPh, (1-C<sub>10</sub>H<sub>7</sub>)<sub>2</sub>CO, or *p*-C<sub>6</sub>H<sub>4</sub>Ph·COPh. CH<sub>2</sub>Ph·COPh gives the α-pinacol (~80%; no β-form), but Ph·[CH<sub>2</sub>]<sub>2</sub>·COPh is unchanged and Ph·[CH<sub>2</sub>]<sub>3</sub>·COPh (prep. from Ph·[CH<sub>2</sub>]<sub>2</sub>·MgBr and PhCN), b.p. 180°/6 mm., 155°/0.2 mm., gives only a small amount of a (?) mixture, b.p. 190°/0.25 mm. 1-Indanone gives only 2-1'-indanylidene-1-indanone, m.p. 142—143°, or in sunlight a small amount of a substance, C<sub>16</sub>H<sub>16</sub>O, m.p. 352—353° (? impure bouxene), but 1-keto-1:2:3:4-tetrahydronaphthalene gives up to 75% of the pinacol, m.p. 192°. CHPh·CH·COPh and CHPh·CH·CMe are unaffected: *p*-OR·C<sub>6</sub>H<sub>4</sub>·COEt (A; R = Me) is unchanged; (A; R = Ac, COEt, or COPr) suffer partial deacylation, but (A; R = Ac) gives also traces of (*p*-OAc·C<sub>6</sub>H<sub>4</sub>·CET·OH)<sub>2</sub>, m.p. 214° (lit. 200°). Benzoin undergoes a reverse Cannizzaro reaction, giving only PhCHO.

R. S. C.

**Phenanthrene derivatives. XI. Acetylation and succinylation of 3-methylphenanthrene.** W. E. Bachmann and G. D. Cortes (*J. Amer. Chem. Soc.*, 1943, **65**, 1329—1334; cf. A., 1940, II, 348).—4-Keto-1:2:3:4-tetrahydrophenanthrene (prep. from 2-C<sub>10</sub>H<sub>7</sub>·[CH<sub>2</sub>]<sub>3</sub>·CO<sub>2</sub>H by PCl<sub>5</sub>·C<sub>6</sub>H<sub>6</sub> and then SnCl<sub>4</sub>; 85% yield; cf. Haworth, A., 1932, 608), m.p. 67—68°, with Me<sub>2</sub>C<sub>2</sub>O<sub>4</sub> etc. gives *Me* 4-keto-1:2:3:4-tetrahydro-3-phenanthrylgyoxylate (85%), m.p. 70—71°, converted by heating with powdered glass at 180° into CO and *Me* 4-keto-1:2:3:4-tetrahydrophenanthrene-3-carboxylate (92%), m.p. 91—92°, which with hot NaOMe·MeOH·C<sub>6</sub>H<sub>6</sub> and then MeI gives *Me* 4-keto-3-methyl-1:2:3:4-tetrahydrophenanthrene-3-carboxylate (89%), m.p. 83.5—84°. Boiling HCl·AcOH·H<sub>2</sub>O then yields 4-keto-3-methyl-1:2:3:4-tetrahydrophenanthrene (88%), m.p. 64—65°, also obtained (89%) from 2-C<sub>10</sub>H<sub>7</sub>·[CH<sub>2</sub>]<sub>2</sub>·CHMe·CO<sub>2</sub>H by PCl<sub>5</sub>·C<sub>6</sub>H<sub>6</sub> and then SnCl<sub>4</sub>, and reduced by boiling Al(OPr<sup>β</sup>)<sub>3</sub>·Pr<sup>β</sup>OH to the 4-OH-compound (91.8%), m.p. 89—93°, which with Pd·C·N<sub>2</sub> at 300—310°, gives 3-methylphenanthrene (I) (95%), m.p. 61—62° (cf. lit.). 1-C<sub>10</sub>H<sub>7</sub>·CH<sub>2</sub>·CH·CH<sub>2</sub> and 30% HBr·AcOH at 40—50° and then room temp. give 1-β-bromo-*n*-propylnaphthalene (75.3%), b.p. 152—156°/1.5 mm., which, when successively added in C<sub>6</sub>H<sub>6</sub> to CHNa(CO<sub>2</sub>Et)<sub>2</sub>·EtOH at 70—80°, boiled, hydrolysed (KOH·EtOH), and decarboxylated (160°), gives γ-1-naphthylisovaleric acid (43%), m.p. 92—93°. Cyclisation (PCl<sub>5</sub>; SnCl<sub>4</sub>) then yields 1-keto- (91%), m.p. 105—106°, and thence [Al(OPr<sup>β</sup>)<sub>3</sub>·Pr<sup>β</sup>OH] 1-hydroxy-3-methyl-1:2:3:4-tetrahydrophenanthrene (85%), m.p. 92—93°, which with Pd·C·N<sub>2</sub> at 300—310° gives (I) (89%). 3-Acetylphenanthrene and aq. (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> in dioxan at 165—167° give 3-phenanthrylacamide (40—80%), m.p. 172—176°, hydrolysed by boiling conc. HCl·AcOH to the acid (76%), m.p. 177—178° (lit. 175—177°), the K salt of which, when distilled with soda-lime at 20 mm., gives >84% of (I). With Ac<sub>2</sub>O and AlCl<sub>3</sub> in PhNO<sub>2</sub> at 0°, (I) gives a mixture, whence, by way of the semicarbazones, 6-acetyl-3-methylphenanthrene (II) (40%), m.p. 95—96° (semicarbazone, m.p. 213—215°), is isolated. However, AcCl·AlCl<sub>3</sub> in PhNO<sub>2</sub> at 0° gives 9-acetyl-3-methylphenanthrene (III), m.p. 90—91°. Structures are proved as follows. Na·Hg·conc. HCl·AcOH·PhMe reduces (II) to 3-methyl-6-ethylphenanthrene (IV) (60%), m.p. 47—48° (picrate, m.p. 156—156.5°), which is also obtained as follows: 3-ethylphenanthrene, Ac<sub>2</sub>O, and AlCl<sub>3</sub> in PhNO<sub>2</sub> at 0° give 6-acetyl-3-ethylphenanthrene, m.p. 86—87° (semicarbazone, m.p. 203—206°), which gives (Willgerodt) 3-ethyl-6-phenanthrylacamide (82%), m.p. 182—183°, and thence, as above, the derived acid (77%), m.p. 110—111°, and (IV) (77%). Similarly (III) gives 3-methyl-9-ethylphenanthrene (V) (56%), m.p. 47—48° (picrate, m.p. 121—122°). 1-C<sub>10</sub>H<sub>7</sub>Et, EtCOCl, and AlCl<sub>3</sub> in CS<sub>2</sub> give 4-propionyl-1-ethylnaphthalene (73%), a liquid, giving in light in Et<sub>2</sub>O the oily α-Br-derivative, which with CHNa(CO<sub>2</sub>Et)<sub>2</sub> etc. gives β-4-ethyl-1-naphthoyl-*n*-butyric acid (48%), m.p. 127—128°; Clemmensen reduction and cyclisation thereof gives 1-keto-3-methyl-9-ethyl-1:2:3:4-tetrahydrophenanthrene (52%), m.p. 97.5—98°, and thence [Al(OPr<sup>β</sup>)<sub>3</sub>·Pr<sup>β</sup>OH] and then Pd·C·N<sub>2</sub> at 310° (V). (CH<sub>2</sub>·CO)<sub>2</sub>O and AlCl<sub>3</sub> in PhNO<sub>2</sub> at 0° convert (I) into γ-keto-γ-6-methyl-3-phenanthryl-*n*-butyric acid (VI), m.p. 184.5—185°

illuminating (II) and Br in Et<sub>2</sub>O gives 6-bromoacetyl-3-methylphenanthrene (82.5%), m.p. 157—158°, which with CHNa(CO<sub>2</sub>Et)<sub>2</sub> etc. gives (VI). (III) gives similarly 9-bromoacetyl-3-methylphenanthrene (83%), m.p. 101—102°, and thence γ-keto-γ-3-methyl-9-phenanthryl-*n*-butyric acid (71%), m.p. 174—175°, which by Clemmensen reduction and subsequent ring-closure [SOCl<sub>2</sub>·Et<sub>2</sub>O·C<sub>6</sub>H<sub>5</sub>N (a drop); SnCl<sub>4</sub>·C<sub>6</sub>H<sub>6</sub>] gives 1-keto-10-methyl-1:2:3:4-tetrahydrotriphenylene (91%), m.p. 80—83°, converted by Al(OPr<sup>β</sup>)<sub>3</sub> and then Pd·C·N<sub>2</sub> at 220° into 2-methyltriphenylene (65%), m.p. 101—102° (picrate, m.p. 191—192°) (Fieser *et al.*, A., 1939, II, 540). Clemmensen reduction of (VI) gives γ-6-methyl-3-phenanthryl-*n*-butyric acid, m.p. (crude) 108—111°, which with PCl<sub>5</sub> and then SnCl<sub>4</sub> gives 1-keto-2'-methyl-1:2:3:4-tetrahydro-5:6-benzanthracene (54%), m.p. 165—168°, and thence, as above, 2'-methyl-1:2-benzanthracene (Cook, A., 1932, 374).

R. S. C.

**2-Methylenecyclohexanone.** C. Mannich (*Ber.*, 1941, **74**, [B], 554—556; cf. A., 1928, 300).—2-Piperidino- or 2-dimethylamino-methylcyclohexanone (or mixtures) when heated in a vac. (~0.3 mm.) gives 2-methylenecyclohexanone (I) (semicarbazone, viscous ~155°, sinters 160°, decomp. ~210°), which can be distilled (high vac.), rapidly dimerises at room temp., and is reduced (H<sub>2</sub>, Pd, MeOH) to 2-methylcyclohexanone. MgMeI and (I) afford 1-methyl-2-methylenecyclohexanol, b.p. 58°/10 mm.

H. B.

**Introduction of the angular methyl group. Preparation of cis- and trans-1-keto-9-methyldecahydronaphthalene.** W. S. Johnson (*J. Amer. Chem. Soc.*, 1943, **65**, 1317—1324).—A three-step process for introducing angular Me into cyclic ketones is described. 2-Benzylidene-6-methylcyclohexanone (improved prep.) with MeI in KOBu<sup>γ</sup>·Bu<sup>γ</sup>OH·N<sub>2</sub> at 0° and then 100° gives 2-benzylidene-6:6-dimethylcyclohexanone (I) (95%), m.p. 79.5—80°, which with Br·CCl<sub>4</sub> gives the dibromide, m.p. 86.5—87.5° [at 140—150° regenerates a little (I)], and with Cl<sub>2</sub>·CS<sub>2</sub> at <0° gives the dichloride, α- (II) (75%), m.p. 82—83°, and β-form (20%), m.p. 83—84°. Boiling NaOEt·EtOH converts (II) into (?) 2-α-ethoxybenzylidene-6:6-dimethylcyclohexanone, an oil, hydrolysed by hot conc. HCl·EtOH to 2-benzoyl-6:6-dimethylcyclohexanone (III), isolated as Cu derivative, m.p. 214—216.5° (decomp.), and obtained in diketo-, m.p. 76—77° (no immediate FeCl<sub>3</sub> colour), and enol forms, m.p. 65—65.5° (purple FeCl<sub>3</sub> colour). Distilling (III) (mixed forms) from 1% NaOH by steam gives ζ-keto-ζ-phenyl-αα-dimethyl-*n*-heptonic acid (46%), m.p. 105—105.5°, 2:2-dimethylcyclohexanone (29%), and BzOH. 1-Ketodecahydronaphthalene, PhCHO, and NaOH in aq. EtOH at room temp. give the 2-CHPh: derivative (IV) (75%), m.p. 91—92° [semicarbazone, m.p. 212.5—214° (decomp.) (bath preheated to 208°)], and some (?) 1-hydroxy-2-α-hydroxybenzyldecahydronaphthalene, m.p. 139.5—140°. MeI·KOBu<sup>γ</sup>·Bu<sup>γ</sup>OH·N<sub>2</sub> converts (IV) into (?) cis- (V), m.p. 104—104.5°, and (?) trans-1-keto-2-benzylidene-9-methyldecahydronaphthalene (VI), m.p. 93.5—94°. The semicarbazone, m.p. 209—210° (decomp.) (bath preheated to 200°), of (VI) is more rapidly formed than is that, m.p. 191—192°, of (V), and (V) and (VI) may be thus separated. Cl<sub>2</sub>·CS<sub>2</sub> at 0°, then boiling NaOEt·EtOH·N<sub>2</sub>, hydrolysis (dil. HCl), and steam distillation from dil. NaOH convert (V) into (?) cis-1-keto-9-methyldecahydronaphthalene (71%), b.p. 116°/14—15 mm. [semicarbazone, m.p. 226—227° (decomp.) (bath preheated to 220°); oxime, dimorphic, m.p. 109—110° and 114.5—115.5°; 2:4-dinitrophenylhydrazone, m.p. 164.5—165.5°; with PhCHO etc. gives (V)] (cf. Cook *et al.*, A., 1937, II, 292), and 1-methyl-2-δ-keto-δ-phenyl-*n*-butylcyclohexane-1-carboxylic acid (VII) (? cis-Me-H), m.p. 131—133°; incomplete hydrolysis gives some (?) cis-1-keto-2-benzoyl-9-methyldecahydronaphthalene [amorphous Cu derivative, m.p. 150—153° (decomp.)]. (VI) yields similarly dichlorides (α form, m.p. 160—161°, was isolated) and thence (?) trans-1-keto-2-benzoyl-9-methyl- (VIII) [amorphous Cu derivative, m.p. 235—238° (decomp.)], and (?) trans-1-keto-9-methyl-decahydronaphthalene, b.p. 119—120°/14—15 mm. [semicarbazone, m.p. 219—220° (decomp.) (bath preheated to 215°), formed rapidly; oxime, m.p. 141.5—142° (cf. *loc. cit.*); 2:4-dinitrophenylhydrazone, m.p. 171.5—172°; with PhCHO gives (VI)], and the (?) trans-isomeride (IX), softens at 162°, m.p. 167—168° (oxime, m.p. 166—166.5°; semicarbazone, m.p. 184—185°), of (VII). The Me ester, m.p. 42—43°, resolidifies, remelts 46—47°, of (IX) with NaOMe·C<sub>6</sub>H<sub>6</sub>·N<sub>2</sub> gives (VIII). M.p. are corr.

R. S. C.

**Synthesis of condensed ring compounds. X. cis-1-Keto-9-methyl-Δ<sup>6</sup>-octahydronaphthalene and cis-10-methyl-1-vinyl-Δ<sup>1:7</sup>-naphthitadiene.** W. Nudenberg and L. W. Butz (*J. Amer. Chem. Soc.*, 1943, **65**, 1436; cf. A., 1942, II, 313, 319).—2-Methyl-Δ<sup>2</sup>-cyclohexenone and (CH<sub>2</sub>·CH)<sub>2</sub> give cis-1-keto-9-methyl-Δ<sup>6</sup>-octahydronaphthalene, b.p. 67°/0.5 mm. [semicarbazone, m.p. 224.8—225° (decomp. from 224°); absorbs 1.88 H], which by way of cis-1-hydroxy-9-methyl-1-acetylenyl-, b.p. 93—94°/0.5 mm., gives 1-hydroxy-9-methyl-1-vinyl-Δ<sup>6</sup>-octahydronaphthalene, b.p. 92°/0.55 mm. With, best, PBr<sub>3</sub>·C<sub>6</sub>H<sub>5</sub>N this yields 9-methyl-1-vinyl-3:4:5:8:9:10-cis-hexahydronaphthalene ["cis-10-methyl-1-vinyl-Δ<sup>1:7</sup>-naphthitadiene"], b.p. 66—67°/0.45 mm. [absorption max. at 2380 Å. (ε 9400) in C<sub>6</sub>H<sub>14</sub> or 2380 Å. (ε 10,000) in EtOH; absorbs 3 H<sub>2</sub>], which with 1:4-O·C<sub>10</sub>H<sub>8</sub>·O at 110° yields (?) 1:2-phthaloyl-13-methyl-1:2:3:5:8:9:10:11:13:14-decahydronaphthalene, m.p. 191.8—192.8°. No details are given.

R. S. C.

**Catalytic hydrogenation of alkyl [aryl] halides. II.** M. Busch, W. Weber, and H. Zink (*J. pr. Chem.*, 1940, [ii], 155, 163—176; cf. A., 1936, 1099).—Hydrogenating (1% Pd-CaCO<sub>3</sub>) 2-bromoanthraquinone in presence of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in 5% KOH-MeOH at 133°/10 atm. gives di-2-anthraquinonyl (I) and anthraquinone (II). 2-Chloroanthraquinone behaves similarly, but less (I) is formed, or, in presence of an excess of N<sub>2</sub>H<sub>4</sub>, only (II). 1-Chloroanthraquinone gives only (II). 9-Chlorobenzanthrone gives di-9-benzanthronyl (13.3%), m.p. 371°, but 3-bromobenzanthrone gives violanthrone (46%). 3:9-Dibromobenzanthrone gives a mixture. 7-Bromoquinoline gives di-7-quinolyl (57.5%), m.p. 171°, and quinoline (36.8%). 9:10-Dibromoanthracene gives only anthracene. 2:7-Dibromofluorene gives fluorene (31%), di-2-fluorenyl (30%), m.p. 310—312°, and impure higher coupling products (12%), m.p. 355—375°. (*p*-C<sub>6</sub>H<sub>4</sub>Br·CH<sub>2</sub>)<sub>2</sub> [prep. from (CH<sub>2</sub>Ph)<sub>2</sub> by Br-I-CCl<sub>4</sub> at 0°; 34% yield], m.p. 216°, gives (CH<sub>2</sub>Ph)<sub>2</sub> (17.8%), 4:4'-di- $\beta$ -phenylethyldiphenyl [bisdibenzyl] (17.4%), m.p. 151°, *p*-terdibenzyl, Ph·[CH<sub>2</sub>]<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·C<sub>6</sub>H<sub>4</sub>·[CH<sub>2</sub>]<sub>2</sub>·Ph (A;  $\alpha$  = 2) (17.0%), m.p. 240—250° (clear at 273°), ? *p*-quaterdibenzyl (A;  $\alpha$  = 3) (12.8%), softens 305°, m.p. 350°, and ? quinquedibenzyl (A;  $\alpha$  = 4) (7.5%), softens ~340°, m.p. >365° (clear >400°). CO(C<sub>6</sub>H<sub>4</sub>Br-*p*)<sub>2</sub> gives similarly CPh<sub>2</sub> (16%), (C<sub>6</sub>H<sub>4</sub>Bz-*p*)<sub>2</sub> (24%), m.p. 214° (216°), ? terbenzophenone (13%), m.p. 326—327° (amorphous phenylhydrazone), ? quaterbenzophenone (11%), sublimes (? m.p.) 387—394°, and products, (3%) decomp. ~400° and (7%) decomp. 440°.

R. S. C.

**Aërobic oxidation of aromatic hydrocarbons in presence of ascorbic acid. Reaction with anthracene and 3:4-benzpyrene.** F. L. Warren (*Biochem. J.*, 1943, 37, 338—341).—In presence of ascorbic acid (I), O<sub>2</sub> oxidises anthracene in aq. 80% COMe<sub>2</sub> in the dark to anthraquinone and 3:4-benzpyrene to the corresponding 5:8- and 5:10-quinones. The reaction is unaffected by Cu<sup>++</sup> (trace) or H<sub>2</sub>O<sub>2</sub> but is inhibited by KCN or HPO<sub>3</sub>. Dihydroxymaleic acid acts like (I). Probably the oxidising agent is a product of autoxidation of (I) (e.g., dehydroascorbic acid or a peroxide thereof), the mechanism being similar to that which occurs during the inhibition by aromatic hydrocarbons of autoxidation of aldehydes.

W. McC.

#### IV.—STEROLS AND STEROID SAPOGENINS.

**Steric junction of rings C and D in steroids.** K. Dimroth and H. Jonsson (*Ber.*, 1941, 74, [B], 520—523).—The semicarbazone, new m.p. 226°, [α]<sub>D</sub><sup>25</sup> +46° in CHCl<sub>3</sub>, of 4-keto-8-methyl-1- $\alpha$ - $\delta$ -trimethyl- $\Delta^8$ -hexenylhydrindane (I) (Windaus *et al.*, A., 1936, 1247; prep. from vitamin-D<sub>2</sub> slightly modified) is hydrolysed (aq. H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) to an isomeride (II) (semicarbazone, m.p. 202°, [α]<sub>D</sub><sup>18</sup> +3.6° in CHCl<sub>3</sub>). Since crude (I) is isomerised by H<sub>2</sub>SO<sub>4</sub> or C<sub>6</sub>H<sub>11</sub>OK to (II), (I) and (II) are the *trans*- and *cis*-derivative, respectively. Hydrogenation (Pd-black, MeOH) of (II) gives its side-chain H<sub>2</sub>-derivative (semicarbazone, m.p. 207°, [α]<sub>D</sub><sup>15</sup> +37° in CHCl<sub>3</sub>), different from that (Windaus *et al.*, A., 1936, 69) of (I). Accordingly rings c and d of the vitamins-D and normal steroids are *trans*.

H. B.

**Deuterocholesterol.** K. Bloch and D. Rittenberg (*J. Biol. Chem.*, 1943, 149, 505—507).—No exchange occurs when suspensions of cholesterol (I) in D<sub>2</sub>O, with or without EtOH, are heated up to 200° in presence of active Pt. Se effects slow introduction of D at 110—230°. Addition of AcOH (containing 60 at.-% D) to the system (I)-D<sub>2</sub>O-Pt at 127° results in D being introduced into the side-chain and ring system of (I); simultaneous destruction of (I) occurs, and the rate of deuteration is roughly parallel to the extent of decomp. The deuterocholesterol, m.p. 148°, [α]<sub>D</sub><sup>26</sup> -3.9° in CHCl<sub>3</sub>, 4.16 at.-% D, is converted into the cholesteryl chloride, and thermally degraded; the H in the resulting mixture of *iso*-octane and -octene shows a higher level of D than that of the hydrocarbon C<sub>10</sub>H<sub>18</sub>, although more isotope was actually present in an equimol. amount of the latter.

A. T. P.

**Marine products. XIII. Sterols from various marine invertebrates.** W. Bergmann, M. J. McLean, and D. Lester (*J. Org. Chem.*, 1943, 8, 271—282).—The broken material is extracted successively with COMe<sub>2</sub> and Et<sub>2</sub>O, the solutions are evaporated, and the residues are hydrolysed (20% KOH in 70% EtOH). The solution is extracted with Et<sub>2</sub>O and the sterols are pptd. with digitonin, the digitonides being subsequently decomposed with C<sub>6</sub>H<sub>5</sub>N. The amount of 7-dehydrosterols present in the crude sterol mixture is determined spectrographically. The homogeneity of the crude sterol is tested by recrystallisation and the prep. of derivatives. When the presence of a mixture is indicated, attempts are made to bring about a separation of the components by means of solubility differences of their bromides. The staghorn coral, *Madrepora cervicornis*, contains a mixture of sterols which are difficult to separate; one of the components gives an acetate, m.p. 176°. The sterols of *Meandra areolata* (A) consist of cholesterol (I) and a sterol showing considerable similarity to clionasterol (II). The gorgonia, *Xiphogorgia* sp., contains a mixture of sterols similar to that present in (A). *Plexaura flexuosa* contains among other unidentified sterols a mono-unsaturated compound, *gorgosterol*, C<sub>30(31)</sub>H<sub>52(54)</sub>O, m.p. 184—185°,

[α]<sub>D</sub><sup>25</sup> -45° (acetate, m.p. 152.6°, becomes opalescent at 140°, [α]<sub>D</sub><sup>25</sup> -56.3°; 3:5-dinitrobenzoate, m.p. 227.5—228.5°, [α]<sub>D</sub><sup>25</sup> -20.3°). The crude sterols of three varieties of sea urchin consist of (I) and of a sterol of the order C<sub>29</sub>, which is similar to sterols of the sitosterol or (II) type. The sea cucumber, *Holothuria princeps*, contains a mixture of sterols similar to that in starfish. The horseshoe crab, *Limulus polyphemus*, contains (I) and a sterol similar to plant sterols or (II). The mixture from the tunicate, *Styela plicata*, contains only (I) and some 7-dehydrosterol. The significance of these results is discussed. M.p. are corr. and [α] are in CHCl<sub>3</sub>.

H. W.

**Conversion of sterols into aromatic compounds. V. Aromatisation of ring A by migration of methyl.** H. H. Inhoffen and G. Zühlsdorff (*Ber.*, 1941, 74, [B], 604—616).—Partly an account of work previously abstracted (A., 1939, II, 17).  $\Delta^1$ :4-Cholestadien-3-one is converted into the phenol, C<sub>27</sub>H<sub>42</sub>O (I), m.p. 145—146° (*loc. cit.*), at 300—320°/3 hr. or by Ac<sub>2</sub>O-conc. H<sub>2</sub>SO<sub>4</sub> at room temp. or Ac<sub>2</sub>O-HI (*d* 1.96) at 100° (bath). (I) gives a dinitrobenzoate (II), m.p. 179—180°, Me ether, m.p. 104—105°, benzeneazo-, m.p. 182—183°, and 2(or 4)-Br<sub>1</sub>-derivative (III), m.p. 83—84° [dinitrobenzoate, m.p. 179—180°, raised to 200—201° when admixed with (II)]. (III) is reduced (Na, aq. EtOH) to (I). Coupling of (I) with Na *p*-nitrophenylantidiazotate in AcOH affords its *p*-nitrobenzeneazo-derivative, m.p. 208—209°, but (III) similarly gives the 4 (or 2)-*p*-nitrobenzeneazo-2(or 4)-acetoxy-derivative, m.p. 229—230° [acetylated (Ac<sub>2</sub>O-C<sub>5</sub>H<sub>5</sub>N) to the corresponding 2(or 4):3-diacetate, m.p. 227—228°], of (I).  $\Delta^1$ :4-Androstadien-17-ol-3-one with Ac<sub>2</sub>O-conc. H<sub>2</sub>SO<sub>4</sub> at room temp. affords 1-methylæstradiol diacetate, m.p. 135—136°, hydrolysed by AcOH-30% H<sub>2</sub>SO<sub>4</sub> at 100° (bath) to the 17-monoacetate, m.p. 199—200° (æstradiol 17-monoacetate can be similarly prepared), and by 5% MeOH-KOH to 1-methylæstradiol (IV), m.p. 231—232°, [α]<sub>D</sub><sup>22</sup> +179.5° in dioxan [Me ether, m.p. 114°; ? benzeneazo-derivative, m.p. 196—197° (diacetate, m.p. 193—194°)]. Absorption spectra for most of the compounds are given. (IV) has no oestrogenic activity.

H. B.

**Steroids with ethylenic linkings between quaternary carbon atoms.**

**I. Oxidation of  $\alpha$ -ergosterol acetate. II. Structure of  $\alpha$ -dihydroergosterol.** H. E. Staveland and G. N. Bollenback (*J. Amer. Chem. Soc.*, 1943, 65, 1285—1289, 1290—1294).—I. Structures ascribed below are proved by the reactions and absorption spectra in EtOH. They provide proof that  $\alpha$ -ergosterol has an ethylenic linking at position 8:14 and that  $\alpha$ -dihydroergosterol is  $\Delta^8$ :22-ergostadien-3-ol.  $\alpha$ -Ergosterol acetate (I) and CrO<sub>3</sub> in AcOH-C<sub>6</sub>H<sub>6</sub> at room temp. give (cf. Reindel, A., 1929, 61; Heilbron, A., 1932, 845) acids and a mixture of neutral products, chromatography of which yields 3-acetoxy- $\Delta^8$ (14)-ergosten-15-one (7%), m.p. 170°, [α]<sub>D</sub><sup>23</sup> +110±3° [absorption max. at 259 mμ. (ε 13,300); semicarbazone, m.p. 199—200°; 2:4-dinitrophenylhydrazine, m.p. 220° (decomp.); with Pd-H<sub>2</sub> (2.1 mols.) in AcOH (not EtOH) gives (I) (80%)], 8:14-epoxy-3-acetoxyergostan-7-one (II) (18%), m.p. 134°, [α]<sub>D</sub><sup>23</sup> -83±3° (gives CO<sub>2</sub> derivatives only after rupture of the epoxy-ring; no absorption at >230 mμ.), 8:14-epoxy-3-acetoxyergostan-15-one (III) (2%), m.p. 208—210°, [α]<sub>D</sub><sup>23</sup> -6.0±1.5° (no absorption at >230 mμ. or 2:4-dinitrophenylhydrazine), (?) 3-acetoxyergostane-8:14-diol-7:15-dione, m.p. 201—202°, [α]<sub>D</sub><sup>23</sup> -69±2°, and a mixture, which, by hydrolysis by boiling conc. HCl-EtOH, acetylation, and then chromatography, yields (?) dehydroergosterol acetate, m.p. 138°, [α]<sub>D</sub><sup>23</sup> -29°, 3-acetoxy- $\Delta^8$ (14)-ergostene-7:15-dione (2%), m.p. 149—151°, [α]<sub>D</sub><sup>24</sup> -24±2° [absorption max. at 255 mμ. (ε 5000); pyridazine derivative, m.p. 220—225° (decomp.)], and 3-acetoxy- $\Delta^8$ (14):9(11)-ergostadien-7-one (IV), m.p. 177°, [α]<sub>D</sub><sup>24</sup> -22±2° [absorption max. at 298 mμ. (ε 5100); 2:4-dinitrophenylhydrazine, m.p. 223° (decomp.)]. Conc. HCl-EtOH at 100° hydrolyses (III) to 3-acetoxy- $\Delta^8$ (14):9(11)-ergostadien-15-one, m.p. 155° [absorption max. at 307 mμ. (ε 10,700); an oil is also formed], and (II) to (IV) (m.p. 176—178°), which with H<sub>2</sub>-Pd in EtOH gives 3-acetoxy- $\Delta^8$ (14)-ergosten-7-one (V), m.p. 155°, [α]<sub>D</sub><sup>22</sup> -62±3° [absorption max. at 262 mμ. (ε 9,800)].

II.  $\gamma$ - is not isomerised to  $\alpha$ -cholestenol by Pd in N<sub>2</sub>, so that the corresponding stability of  $\alpha$ -dihydroergosterol is without significance. Chromatography of the neutral products formed from  $\alpha$ -dihydroergosterol acetate by CrO<sub>3</sub> in AcOH-C<sub>6</sub>H<sub>6</sub> at room temp. gives 8:9- (VI) (16%), m.p. 223—225°, [α]<sub>D</sub><sup>24</sup> -46±2° [no absorption at >230 mμ.]; 2:4-dinitrophenylhydrazine, m.p. 209° (decomp.), and 8:14-epoxy-3-acetoxy- $\Delta^22$ -ergosten-7-one (VII) (18%), m.p. 155°, [α]<sub>D</sub><sup>24</sup> -99±3° [no absorption at >230 mμ.]; 2:4-dinitrophenylhydrazine, m.p. 218° (decomp.), and a mixture, which by hydrolysis by hot conc. HCl-EtOH gives ketones (Girard's reagent T), separated by chromatography (after acetylation) into 3-acetoxy- $\Delta^8$ (14):9(11):22-ergostatrien-7-one (VIII), m.p. 187—189°, [α]<sub>D</sub><sup>24</sup> -47±2.5° [absorption max. at 300 mμ. (ε 5000)]; 2:4-dinitrophenylhydrazine, m.p. 222° (decomp.), and 3-acetoxy- $\Delta^8$ (9):22-ergostadien-7-one (IX) (4%), m.p. 206—208°, [α]<sub>D</sub><sup>24</sup> -53±2° [absorption max. at 252 mμ. (ε 10,100)]. Conc. HCl-EtOH converts (VI) or (VII) into (VIII). Hydrogenation (Pd) in EtOH converts (VI) into 8:9-epoxy-3-acetoxyergostan-7-one, m.p. 211°, [α]<sub>D</sub><sup>23</sup> -38±3°, (VII) into (II) (m.p. 132—133°, [α]<sub>D</sub><sup>23</sup> -77±4°), (VIII) into (V), and (VIII) or (IX) (in AcOH) into (I) and 3-acetoxyergostan-7-one, m.p. 183—184°, [α]<sub>D</sub><sup>23</sup> -36±1.5° [semicarbazone, m.p. 225—228°; 2:4-dinitrophenyl-

hydrazone, m.p. 216° (decomp.), hydrolysed to *ergostan-3-ol-7-one*, m.p. 154°. (V) is not isomerised by conc. HCl-EtOH.  $[\alpha]$  (both parts) are in CHCl<sub>3</sub>. R. S. C.

Saturated and unsaturated steroid ketones.—See B., 1943, III, 255.

Cyclic ketals of 3-keto-17-hydroxy-17-acetylenylcyclopentanoperhydrophenanthrenes.—See B., 1943, III, 255.

Compound C, C<sub>21</sub>H<sub>32</sub>O<sub>3</sub>, m.p. 268°,  $[\alpha]_D -48^\circ (\pm 2^\circ)$  to  $-39^\circ (\pm 2^\circ)$  in C<sub>6</sub>H<sub>5</sub>N [oxime, m.p. 238—239° (decomp.)] (? testalolone), and substance E, C<sub>21</sub>H<sub>32</sub>O<sub>3</sub>, m.p. 270—280°,  $[\alpha]_D +3.5^\circ \pm 3.5^\circ$  in CHCl<sub>3</sub>, from swine testis.—See A., 1943, III, 742.

Sterols. CLVIII. Sapogenins. LXX. Structure of lilagenin. R. E. Marker, R. B. Wagner, C. H. Ruof, D. P. J. Goldsmith, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1943, 65, 1434).—*Lilium humboldtii* yields lilagenin, new formula C<sub>27</sub>H<sub>42</sub>O<sub>4</sub> (cf. A., 1941, II, 50), m.p. 242—246° (diacetate, m.p. 153—155°), which absorbs Br slowly and with 2N-HCl-EtOH gives yuccagenin (A., 1943, II, 304), from which it thus differs only in the configuration of the side-chain. R. S. C.

Saponins and sapogenins. XXII. Composition and constitution of bethogenin. C. R. Noller and M. R. Parusch (*J. Amer. Chem. Soc.*, 1943, 65, 1435—1436).—Bethogenin (I) is shown to be C<sub>28</sub>H<sub>44</sub>O<sub>4</sub> (cf. A., 1943, II, 99) by analysis of (I), its acetate, and benzoate. The additional C is present as Me, possibly as enol Me ether, since, although NH<sub>2</sub>OH-EtOH-C<sub>6</sub>H<sub>5</sub>N introduces 2 N, (I) has no CO absorption [rise from 3500 to 2300 A., inflexion at 2850 A. ( $\epsilon$  0.3)] until after treatment with HBr-AcOH [then a max. at 2850 A. ( $\epsilon$  1.77)]. R. S. C.

## V.—TERPENES AND TRITERPENOID SAPOGENINS.

Dependence of optical rotatory power on chemical constitution.

XXI. Rotatory dispersion of stereoisomeric hydroxyphenylaminomethylenecamphors and their acetylated and benzoylated derivatives. B. K. Singh and S. C. Sen (*J. Indian Chem. Soc.*, 1943, 20, 1—10).—d- and l-, m.p. 180—182°,  $[\alpha]_{5461}^{25} = 436.2^\circ$  in EtOH (*Ac*, m.p. 131—132°,  $[\alpha]_{5461}^{25} +266.3^\circ$  and  $-267.8^\circ$  in EtOH, and Bz derivative, an oil), and dl-o-, m.p. 164—165° (*Ac* derivative, m.p. 140—142°, d- and l-, m.p. 165°,  $[\alpha]_{5461}^{25} +417.1^\circ$  and  $-415.9^\circ$  in EtOH (*Ac*, m.p. 140—142°,  $[\alpha]_{5461}^{25} \pm 181.1^\circ$  in EtOH, and Bz derivative, an oil), and dl-m-, m.p. 165°, and d- and l-, m.p. 158—160°,  $[\alpha]_{5461}^{25} +450.5^\circ$  and  $-450.0^\circ$  in EtOH (*Ac*, m.p. 220—222°,  $[\alpha]_{5461}^{25} \pm 190.3^\circ$  in EtOH, and Bz derivative, m.p. 236—237°  $[\alpha]_{5461}^{25} \pm 6.20^\circ$  in EtOH), and dl-p-hydroxyanilinomethylenecamphor, m.p. 150—152° (*Ac* derivative, m.p. 195—197°), are prepared from hydroxymethylenecamphor in MeOH and NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH in AcOH at room temp.  $[\alpha]$  of these for 6  $\lambda$  in 5 solvents have been determined [and can be expressed as  $k/(\lambda^2 - \lambda_0^2)$ ] and compared with vals. for anilino- and methyl-, chloro-, bromo-, and iodo-anilino-methylenecamphor. The influence on  $[\alpha]$  of the nature and position of substituents, the nature of the solvent, and of acetylation and benzoylation is discussed. A. Li.

Cardanol derivative.—See B., 1943, II, 212.

## VI.—HETEROCYCLIC.

Tetrahydrofurfuryl ethers.—See B., 1943, II, 283.

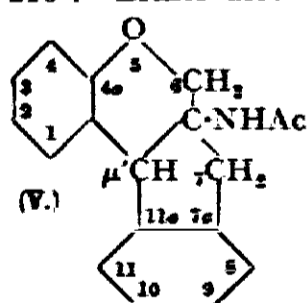
3-Chloro-2-ethoxy-2-methyltetrahydrofuran.—See B., 1943, II, 277.

Condensations by sodium. XXVII.—See A., 1943, II, 345.

Vitamin-E. XII. Synthesis of  $\alpha$ -chloro- $\gamma$ -tetramethylhexadecan- $\gamma$ -ol and its condensation with trimethylquinol to form  $\alpha$ -tocopherol. L. I. Smith and J. A. Sprung (*J. Amer. Chem. Soc.*, 1943, 65, 1276—1283; cf. A., 1943, II, 240).—Pure  $\alpha$ -tocopherol is synthesised from citral in 4—5% over-all yield. Adding Na and then EtBr to [CH<sub>2</sub>]<sub>2</sub>(OH)<sub>2</sub> in xylene at 115—120° and then heating at 120° gives 58—62% of OEt[CH<sub>2</sub>]<sub>2</sub>·OH, b.p. 157—163° (38% obtained from Cl[CH<sub>2</sub>]<sub>2</sub>·OH by NaOEt). Similarly are prepared OMe[CH<sub>2</sub>]<sub>2</sub>·OH (64% obtained in absence of xylene), b.p. 148—149°, and CH<sub>2</sub>Ph·O[CH<sub>2</sub>]<sub>2</sub>·OH (73%), b.p. 145—150°/13 mm. Thence PBr<sub>3</sub> in Et<sub>2</sub>O at  $>60^\circ$  gives OR[CH<sub>2</sub>]<sub>2</sub>·Br, in which R = Et (55—65%), b.p. 147—150°/760 mm., 86—87°/100 mm., and Me (27%), b.p. 131—133°; PBr<sub>3</sub> in NPhMe<sub>2</sub> at 0° and then 50° gives  $\gamma$ -benzyl-oxy-n-propyl bromide (34%), b.p. 130—132°/8 mm.; PCl<sub>5</sub> in C<sub>6</sub>H<sub>5</sub>N at 0° and then 75° gives OEt[CH<sub>2</sub>]<sub>2</sub>·Cl (67%), b.p. 125—128°. Saturating freshly distilled COMe·CH<sub>2</sub>·CH<sub>2</sub> with dry HCl at 0° and keeping at room temp. gives 67% of Cl[CH<sub>2</sub>]<sub>2</sub>·COMe (I), b.p. 48—50°/15 mm., converted by quinoline or KOH-EtOH into impure mixed dienes, b.p. 65—75°, which give no solid product with 2:3:5:1:4-C<sub>5</sub>HMe<sub>5</sub>(OH)<sub>2</sub> (II). For the following synthesis  $\phi$ -ionone (III) should be prepared from purified citral and COMe<sub>2</sub> (Russell *et al.*, *Org. Syntheses*, 1943, 23, 78) and purified by way of the NaHSO<sub>3</sub> compound (45% yield), otherwise yields drop greatly. Adding OR[CH<sub>2</sub>]<sub>2</sub>·Br and (III) to Mg in Et<sub>2</sub>O, the reaction having been started by a trace of I or EtBr, gives  $\alpha$ -ethoxy- (52%), b.p. 162—165°/13 mm. (the chloride gives 46%), impure  $\alpha$ -methoxy-

[53.3% from impure (III)], b.p. 150—160°/3 mm., and  $\alpha$ -benzyloxy- $\delta\theta\mu$ -trimethyl- $\Delta^7\epsilon\eta\lambda$ -n-tridecatetraene (49%), b.p. 210—220° (some decomp.)/3 mm. H<sub>2</sub>-Raney Ni at 125—150°/2000 lb. then yields  $\alpha$ -ethoxy- $\delta\theta\mu$ -trimethyl-n-tridecane (82%), b.p. 138—140°/3 mm. (impurities hinder the hydrogenation), converted [best (96%) by dry HBr at 150° in a sealed tube] into  $\delta\theta\mu$ -trimethyl-n-tridecyl bromide (IV), b.p. 138—140°/3 mm. The saturated Me ether (similarly prepared) reacts more readily, the CH<sub>2</sub>Ph ether still more so. (IV), freed from alcohol by H<sub>2</sub>SO<sub>4</sub>, yields a Grignard reagent in Et<sub>2</sub>O, which with MeCHO at 0° and then the b.p. gives  $\zeta\epsilon$ -trimethyl-n-pentadecan- $\beta$ -ol (70%), b.p. 150—155°/3 mm., oxidised by Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-AcOH-H<sub>2</sub>SO<sub>4</sub>-C<sub>6</sub>H<sub>5</sub> at 40—50° to the corresponding ketone ("phytol ketone") (75%), b.p. 150—152°/3 mm., identical with that derived from natural phytol.  $\alpha$ -Chloro- $\gamma$ -methyl-n-pentan- $\gamma$ -ol [prep. by adding (I) to MgEtBr-Et<sub>2</sub>O at 0°; 51% yield], b.p. 104—105°/50 mm., (II), and ZnCl<sub>2</sub> in boiling AcOH give 6-hydroxy-2:5:7:8-tetramethyl-2-ethylchroman. n-C<sub>12</sub>H<sub>25</sub>Br with CH<sub>2</sub>·CH·COMe and Mg gives a gel, but with Mg and (I) gives impure  $\alpha$ -chloro- $\gamma$ -methyl-n-pentadecan- $\gamma$ -ol (34.5%), b.p. 165—170°/3 mm. The Grignard reagent from impure (IV) with (I) in Et<sub>2</sub>O at 0° and then the b.p. gives  $\alpha$ -chloro- $\gamma$ - $\eta\lambda$ -tetramethyl-n-hexadecan- $\gamma$ -ol (38%), b.p. 173—175°/2 mm., which with (II) and ZnCl<sub>2</sub> in AcOH at 115° and then the b.p. gives 70% of  $\alpha$ -tocopherol (fully identified). Br[CH<sub>2</sub>]<sub>2</sub>·OAc (prep. from Br[CH<sub>2</sub>]<sub>2</sub>·OH by AcCl) reacts sluggishly with (III) and Mg in Et<sub>2</sub>O and gives only polymerides. R. S. C.

Brazilin and haematoxylin. XVII. Synthesis of  $\mu$ -aminochromindane. P. Pfeiffer and H. Epler (*Annalen*, 1940, 545, 263—286).—OPh·CH<sub>2</sub>·O·CH<sub>2</sub>·Ph (I), b.p. 167°/1.5 mm., m.p. 43°, is not readily obtained from OPh·CH<sub>2</sub>·COCl and CH<sub>2</sub>Ph·MgCl but is prepared readily from the Grignard reagent and OPh·CH<sub>2</sub>·CN. It is not brominated in AcOH or CCl<sub>4</sub> alone but in presence of CaCO<sub>3</sub> affords CHPhBr OPh·CH<sub>2</sub> ketone, m.p. 83—90° (slight decomp.), which is not converted into an oxazole derivative by NH<sub>2</sub>Bz in presence of NaOAc or altered by AlCl<sub>3</sub> in Et<sub>2</sub>O. (I) when heated under CO<sub>2</sub> at 80°/40 atm. with KCN and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in aq. EtOH affords 5-benzyl-5-phenoxy-methylhydantoin, m.p. 197°, slowly hydrolysed by 40% KOH at 175° to  $\alpha$ -amino- $\beta$ -phenoxy- $\beta'$ -phenylisobutyric acid (II) (+AcOH), m.p.  $\sim 210^\circ$  (decomp.) (hydrochloride, decomp. 240°), purified through the Cu salt, C<sub>22</sub>H<sub>22</sub>O<sub>4</sub>N<sub>2</sub>Cu. The *Ac* derivative (III), m.p. 201.5°, of (II) is transformed by short treatment with AlCl<sub>3</sub>-NaCl at 160° into 3-acetamido-3-benzylchromanone (IV), m.p. 148°, in very poor yield. Much better results are obtained by controlled treatment of (III) with syrupy H<sub>3</sub>PO<sub>4</sub>, whereby also an unidentified substance, m.p. 183°, and a fulvene derivative, C<sub>16</sub>H<sub>10</sub>O, m.p. 198°, are formed. (IV) does not give an oxime. (IV) cannot be reduced by AcOH-HI but is converted by Na-Hg in an aq. alcoholic phosphate buffer under polarographic control into 3-acetamido-3-benzylchromanol,  $\alpha$ -form, m.p. 146.5° (also +1Et<sub>2</sub>O),  $\beta$ -form, m.p. 219°. Either alcohol is transformed by syrupy H<sub>3</sub>PO<sub>4</sub> at  $>140^\circ$



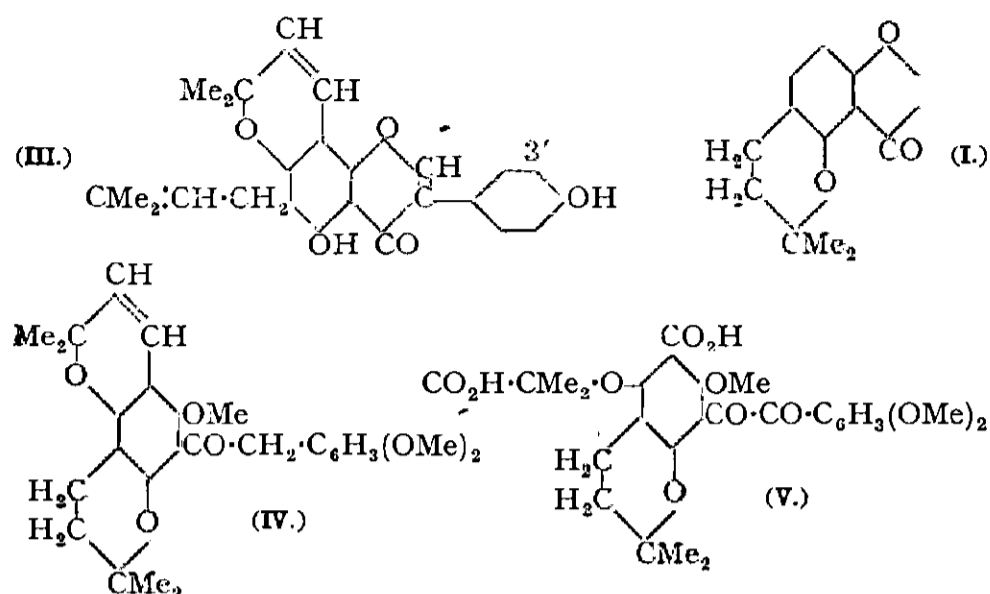
into  $\mu$ -acetamidochromindane (V), m.p. 193°. Hydrolysis of (V) is difficult and best effected with HCl in aq. EtOH at 120°, thereby yielding  $\mu$ -aminochromindane hydrochloride. 3:4-Dimethoxybenzyl 2:3-dimethoxyphenoxy-methyl ketone is transformed by KCN and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in aq. EtOH under CO<sub>2</sub> at 97°/8 atm. into 5-3":4"-dimethoxybenzyl-5-2':3'-dimethoxyphenoxy-methylhydantoin, m.p. 211°, which is hydrolysed by boiling 20% KOH to  $\alpha$ -amino- $\beta$ -2:3-dimethoxyphenoxy- $\beta'$ -3':4'-dimethoxyphenylisobutyric acid, m.p. 184.5° (also +1H<sub>2</sub>O). This is converted by HCl and NaNO<sub>2</sub> into the corresponding  $\alpha$ -OH-acid (+1H<sub>2</sub>O, m.p. 107—113°), also obtained by action of fuming HCl-AcOH at room temp. and then at the b.p. on the  $\alpha$ -OH-nitrile. H. W.

Xanthhydrol as a reagent for the characterisation of primary amides. R. F. Phillips and B. M. Pitt (*J. Amer. Chem. Soc.*, 1943, 65, 1355—1357).—Xanthhydrol + an amide in AcOH-EtOH-H<sub>2</sub>O at 85° or AcOH at room temp. of 100° give  $\sim 55\%$  (more in AcOH alone) of 9-acylamidoxanthenes, useful for identification of the amide (cf. Adriani, A., 1916, i, 155). Di- and tri-chloroacet-, salicyl-, ox-, and picr-amide, guanidine, and cyanoguanidine do not react. CH<sub>2</sub>Cl·CO·NH<sub>2</sub> reacts slowly. HCO·NH<sub>2</sub> sometimes, but not always, gives the compound, m.p. 184°. NHPAc does not react, so that probably a CO·NH<sub>2</sub> is essential. 9-Acet-, m.p. 238—240°, -propion-, m.p. 210—211°, -n-, m.p. 185—187°, and -iso-buty-, m.p. 210—211°, -n-, m.p. 166—167°, and -iso-valer-, m.p. 182—183°, -n-, m.p. 159—160°, and -iso-hex-, m.p. 159—160°, -n-hept-, m.p. 154—155° (153—154°), -n-oct-, m.p. 147.5—148.5°, -palmit-, m.p. 140—142°, -stear-, m.p. 139—141°, -phenylacet-, m.p. 194—195°, - $\beta$ -phenylpropion-, m.p. 188—189°, - $\alpha$ -phenylbutyr-, m.p. 157—158°, -chloroacet-, m.p. 208—209°, -cyanoacet-, m.p. 222—223°, -benz-, m.p. 222.5—223.5°, -o-, m.p. 199—200.5°, and -p-tolu-, m.p. 224—225°, -p-nitrobenz-, m.p. 231—233°, and -2'-furo-, m.p. 209—211°, -amidoxanthen, 9-succin-, m.p. 245—247°, and 9-phthal-, m.p. 176—177°, -imidoxanthen are prepared. R. S. C.

Crystalline complexes of arsenic, antimony, and bismuth trichlorides with dioxan.—See A., 1943, I, 282.

Esters of 1:4-dioxan-2:3-diol.—See B., 1943, II, 277.

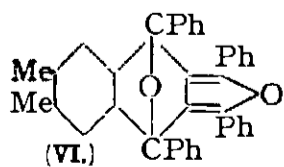
Structures of osajin and pomiferin. M. L. Wolfrom, G. F. Johnson, W. D. Harris, and B. S. Wildi (*J. Amer. Chem. Soc.*, 1943, **65**, 1434—1435).—Fusion of isoosajin (I) or isopomiferin (II) with alkali (no details) gives COMe<sub>2</sub> and 2:2-dimethylchroman-5:7-diol. Osajin (III) and (I) thus have the annexed structure. Pomiferin and



(II) are the corresponding 3'-OH-derivatives. isoPomiferin Me<sub>3</sub> ether (IV) and KMnO<sub>4</sub> give an acid (V), m.p. 204—205° (decomp.) (Me<sub>2</sub> ester, m.p. 133.5—134°). R. S. C.

Dyes derived from acenaphthenequinone. VIII. (6-Methyl)thionaphthen-acenaphthylene-indigos. S. K. Guha (*J. Ind. Chem. Soc.*, 1943, **20**, 37—39).—1-(6-Methyl)thionaphthenacenaphthyleneindigo, m.p. 304°, is formed from accenaphthenequinone and 2-hydroxy-6-methylthionaphthen in boiling AcOH-conc. HCl. 1-(6-Methyl)thionaphthen-8'-(3'-chloro)-, m.p. 274°, -8'-(3'-bromo)-, m.p. 264—265°, and -8'-(1'-methoxy)-, m.p. 300°, -acenaphthyleneindigos are prepared similarly. All dye cotton red from a hyposulphite vat and wool red from an acid bath. 6:6'-Dimethylthioindigo has been prepared from 2-hydroxy-6-methylthionaphthen by oxidation with K<sub>2</sub>Fe(CN)<sub>6</sub>. It dyes cotton and wool red from hyposulphite and acid baths respectively. J. H. BA.

Diene synthesis with an isobenzthiophen. C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 1283—1285).—(CH<sub>2</sub>:CPh)<sub>2</sub> and trans-(CHBz)<sub>2</sub>, much better in EtOH than in xylene, give 4:5-dibenzoyl-1:2-diphenyl-Δ<sup>1</sup>-cyclohexene (I), m.p. 154—155°, which with S at 200—220° gives 2:5:4':5'-tetraphenyl-3:4-benzthiophen [1:3:5:6-tetraphenylisobenzthiophen] (60—70%), m.p. 227—228°. This is yellow, has a strong greenish fluorescence (solid and solution), does not add MeI, and gives no sulphone, but with CrO<sub>3</sub> or HNO<sub>3</sub> in AcOH gives 4:5-dibenzoyl-1:2-diphenylbenzene [4:5-dibenzoyl-o-terphenyl] (II), m.p. 196—197°, and with (CH<sub>3</sub>CO)<sub>2</sub>O (III) at the b.p. gives 1:4-endothio-1:4:6:7-tetraphenyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic anhydride (IV), m.p. 245° (decomp.). (IV) dissociates at the m.p., does not react with p-C<sub>6</sub>H<sub>4</sub>Me-SO<sub>3</sub>Me at 200°, MeI in MeNO<sub>2</sub> or at 150°, or Pb salts, but with boiling HCl-xylene gives H<sub>2</sub>S and an ester, hydrolysed by boiling aq. NaOH to 1:4:5:7-tetraphenyl-naphthalene-2:3-dicarboxylic acid (V), m.p. 310° (decomp.) [anhydride, m.p. 310° (decomp.)]. With a little H<sub>3</sub>PO<sub>4</sub> in Ac<sub>2</sub>O at 110—120°, (I) gives 1:2:4:5-tetraphenyl-3:6-dihydrobenzofuran, m.p. 276—277°, converted by Br-NaOAc-AcOH into (II), which is also obtained from (IV) by Br. Zn dust reduces (II) in boiling AcOH or NaOH-EtOH to 1:2:4:5-tetraphenylisobenzofuran, m.p. 286—287° (and a white substance, m.p. 248—250°), converted by (III) in hot C<sub>6</sub>H<sub>6</sub> into 1:4-epoxy-1:4:6:7-tetraphenyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic anhydride, m.p. 246—247° (yellow owing to dissociation), which with dry HCl-MeOH and then aq. NaOH gives (V). 1:2-Diphenyl-4:5-dimethylisobenzofuran and trans-(CHBz)<sub>2</sub> in boiling EtOH give 1:4-epoxy-2:3-dibenzoyl-1:4-diphenyl-6:7-dimethyl-1:2:3:4-tetrahydronaphthalene, m.p. 169°, dissociated (mol. wt.) in boiling C<sub>6</sub>H<sub>6</sub> and reduced by Zn dust in boiling AcOH to 1':4'-epoxy-2:5:1':4'-tetraphenyl-6':7'-dimethyl-1':4'-dihydronaphtha-2':3':3':4'-furan (VI), m.p. 194—195°. With p-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O, (VI) gives an adduct, C<sub>44</sub>H<sub>32</sub>O<sub>4</sub>, m.p. 145—146°, and with (III) gives, by hydrolysis etc., an acid, C<sub>42</sub>H<sub>32</sub>O<sub>6</sub>, m.p. 271—272°, not reconverted into (VI) by Zn(OAc)<sub>2</sub> or AcOH. 1-Benzoyl-2-phenylisobenzofuran and (III) give 1:4-epoxy-1-benzoyl-4-phenyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic anhydride, m.p. 105—106°. R. S. C.



Synthesis of sulphanilamide derivatives of thianthren. P. C. Guha and V. M. Dokras (*Current Sci.*, 1943, **12**, 119).—Hydrolysis (HCl) of 2:6-diacetamido- yields 2:6-diamino-thianthren, m.p. 120° (p-NHAc-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub> derivative, decomp. 180°). F. R. G.

Thioketonic esters.—See A., 1943, II, 327.

Piperidinoethyl dodecyl ether.—See B., 1943, II, 273.

Double intramolecular alkylation. V. Prelog. I. Alkyl derivatives of 1-azadicyclo-[1:2:2]-heptane. V. Prelog, S. Heimbach, and A. Rezek. II. Synthesis of 2-methyl- and 2-ethyl-quinuclidine. V. Prelog, S. Heimbach, and E. Cerkovnikov. III. Synthesis of 3-methyl- and 3-ethyl-quinuclidine. V. Prelog, N. Šostarič, and E. Guštak. IV. 1-Azadicyclo-[0:5:5]-dodecane. V. Prelog and B. Schönbaum. V. 2-Substituted quinuclidine derivatives. V. Prelog and E. Cerkovnikov (*Annalen*, 1940, **545**, 229—242, 243—247, 247—256, 256—259, 259—262).—I. Tetrahydro-4-pyrone, CHMeBr·CO<sub>2</sub>Et, and Zn turnings in boiling C<sub>6</sub>H<sub>6</sub> afford Et α-4-hydroxy-4-tetrahydropyranylpropionate, b.p. 100°/0.06 mm., dehydrated by boiling Ac<sub>2</sub>O containing a little conc. H<sub>2</sub>SO<sub>4</sub> to α-4-tetrahydropyranylidene-4-propionate, b.p. 117—120°/11 mm., which is hydrogenated to Et α-4-tetrahydropyranylpropionate, b.p. 116—117°/13 mm.; the free acid (I) has b.p. 129—130°/0.4 mm., m.p. 54—55°. (I) is transformed by NaN<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in presence of CHCl<sub>3</sub> into α-amino-α-4-tetrahydropyranylethane (II), b.p. 81°/13 mm., 78°/11 mm. (picrate, m.p. 152—153°), also obtained by reduction (Na-EtOH) of tetrahydropyranyl Me ketoxime, m.p. 54—55°. The hydrobromide of (II) is transformed by 69% HBr at 100° into α-bromo-δ-amino-γ-β'-bromoethylpentane hydrobromide, m.p. 147°, converted by gradual addition of its aq. solution to 0.1N-NaOH at 50° into 7-methyldicyclo-[1:2:2]-aza-1-heptane (III), b.p. 43°/11 mm., also obtained from αδ-dibromo-γ-β'-bromoethylpentane and 20% NH<sub>3</sub>-MeOH at 120—130°. (III) gives a hydrochloride, m.p. 275° (decomp.), platinichloride, m.p. 231° (decomp.), picrate, m.p. 290—293°, picrolonate, m.p. 225—226°, and methiodide, m.p. 325°. A similar series of experiments starting from CHBrEt·CO<sub>2</sub>Et gives Et α-4-hydroxy-4-tetrahydropyranyl-n-butyrate, b.p. 113—117°/0.2 mm., Et α-4-tetrahydropyranylidene-n-butyrate, b.p. 124—125°/10 mm., Et α-4-tetrahydropyranyl-n-butyrate, b.p. 119—120°/10 mm., and the corresponding acid (IV), b.p. 125—130°/0.04 mm. (anilide, m.p. 155°). Et<sub>2</sub> 4-tetrahydropyranylmalonate, EtI, and NaOEt afford Et<sub>2</sub> ethyl-4-tetrahydropyranylmalonate, b.p. 162—164°/13 mm., hydrolysed to the dicarboxylic acid, m.p. 174—175°, which is decarboxylated at 200° to (IV). Conc. H<sub>2</sub>SO<sub>4</sub> and NaN<sub>3</sub> convert (IV) at 50° into α-amino-α-4-tetrahydropyranylpropane, b.p. 100—101°/15 mm. (picrate, m.p. 168°; hydrobromide, m.p. 167—168°), also obtained by reduction of 4-tetrahydropyranyl Et ketoxime and converted by 68% HBr at 100° into α-bromo-δ-amino-γ-β'-bromoethylhexane hydrobromide, m.p. 156—157°, which with 0.1N-NaOH at 50° affords 7-ethyldicyclo-[1:2:2]-aza-1-heptane [hydrochloride, m.p. 239—240°; platinichloride, m.p. 242° (decomp.); picrate, m.p. 198—199°; picrolonate, m.p. 233—233.5°; styphnate, m.p. 170°; methiodide, m.p. 271° (decomp.)]. This base is not identical with that described previously (A., 1939, II, 457); the latter substance does not appear to be homogeneous and probably results from CHEtBr·CH([CH<sub>2</sub>]<sub>2</sub>Br)<sub>2</sub> and NH<sub>3</sub> by an abnormal reaction. Similarly CMe<sub>2</sub>Br·CO<sub>2</sub>Et yields Et α-4-hydroxy-4-tetrahydropyranylisobutyrate, b.p. 100—110°/0.06 mm., Et α-4-tetrahydropyranylideneisobutyrate, b.p. 124—126°/12 mm., Et α-4-tetrahydropyranylisobutyrate, b.p. 118—122°/13 mm., and the corresponding acid, m.p. 90—91. This is converted into β-amino-β-4-tetrahydropyranylpropane, b.p. 98—100°/16 mm., the hydrobromide, m.p. 203°, of which is transformed by 68% HBr at 100° into α-bromo-δ-amino-δ-methyl-γ-β'-bromoethylpentane hydrobromide, m.p. 169—170°, from which is derived 7:7'-dimethyldicyclo-[1:2:2]-aza-1-heptane [hydrochloride, m.p. 299—300° (decomp.); platinichloride, m.p. 233—234° (decomp.); picrate, carbonises at >290°]; the PhSO<sub>2</sub>Cl used in purifying the crude base forms 1-benzenesulphonyl-2:2-dimethyl-3-vinylpyrrolidine or 1-benzenesulphonyl-4-isopropylidenepiperidine, m.p. 83°.

II. 4-Tetrahydropyranylacetyl chloride, b.p. 110—111°/15 mm., is converted by ZnMeI into 4-tetrahydropyranylacetone, b.p. 102—105°/10 mm. (2:4-dinitrophenylhydrazones, m.p. 135—136°); the corresponding oxime, b.p. 150°/14 mm., m.p. 37—38°, is reduced (Na-EtOH) to β-amino-α-4-tetrahydropyranylpropane, b.p. 93°/12 mm. (picrate, m.p. 184°), which is transformed by 70% HBr at 100° into α-bromo-ε-amino-γ-β'-bromoethylhexane hydrobromide (corresponding picrate, m.p. 150—150.5°). This with 0.1N-NaOH at 50° yields 2-methyldicyclo-[2:2:2]-aza-1-octane (2-methylquinuclidine), b.p. 161° (hydrochloride, m.p. 327°; platinichloride, m.p. 216—217°; picrate, m.p. 286°; styphnate, m.p. 208.5°; methiodide, m.p. 346.5° (decomp.); picrolonate, m.p. 226°). Similarly, α-4-tetrahydropyranylbutan-β-one, b.p. 109°/9 mm. (2:4-dinitrophenylhydrazones, m.p. 117—118°), gives a non-cryst. oxime, b.p. 148—154°/8 mm., which is reduced to β-amino-α-4-tetrahydropyranylbutane, b.p. 104°/12 mm. (picrate, m.p. 148°). This affords α-bromo-ε-amino-γ-β'-bromoethylheptane hydrobromide, m.p. 123°, which is converted into 2-ethylquinuclidine, b.p. 180—181° (hydrochloride, m.p. 239°; platinichloride, m.p. 227°; picrate, m.p. 170—171°; picrolonate, m.p. 219°; methiodide, m.p. 290—290.5°).

III. 4-Tetrahydropyranyl Me ketone, CH<sub>2</sub>Br·CO<sub>2</sub>Et, and Zn turnings in boiling C<sub>6</sub>H<sub>6</sub> afford Et β-hydroxy-β-4-tetrahydropyranyl-n-butyrate, dehydrated by KHSO<sub>4</sub> at 90° to Et β-4-tetrahydropyranylcrotonate, b.p. 136°/16 mm., which is hydrogenated (after repeated

distillation over Pt-black in vac.) to *Et*  $\beta$ -4-tetrahydropyranylbutyrate, b.p. 130—131°/12 mm., hydrolysed to the acid, b.p. 135—140°/0.4 mm., m.p. 64.5—65°. This is converted by  $\text{NaN}_3$  and conc.  $\text{H}_2\text{SO}_4$  in presence of  $\text{CHCl}_3$  into  $\alpha$ -amino- $\beta$ -4-tetrahydropyranylpropane, b.p. 102°/14 mm., which yields  $\epsilon$ -bromo- $\alpha$ -amino- $\beta$ -methyl- $\gamma$ - $\beta'$ -bromoethylpentane hydrobromide, m.p. 163—165°, and thence 3-methylquinuclidine [3-methyldicyclo-[2:2:2]-aza-1-octane], b.p. 171° [hydrochloride, m.p. 312—324° (sealed capillary) according to the rate of heating; platinichloride, m.p. 219°; picrate, m.p. 227°; methiodide, m.p. 316° (decomp.); picrolonate, m.p. 205—206°]. 4-Tetrahydropyranyl *Et* ketone gives a product which readily loses  $\text{H}_2\text{O}$  to form *Et*  $\beta$ -4-tetrahydropyranyl- $\Delta^{\alpha}$ -pentenoate, b.p. 92—95°/0.2 mm., reduced (PtO<sub>2</sub> in EtOH) to *Et*  $\beta$ -4-tetrahydropyranylvaleate, b.p. 139—143°/11 mm., which is hydrolysed to the acid, b.p. 129—131°/0.02 mm. This is converted successively into  $\alpha$ -amino- $\beta$ -4-tetrahydropyranylbutane, b.p. 113°/14 mm.,  $\alpha$ -bromo- $\delta$ -aminomethyl- $\gamma$ - $\beta'$ -bromoethylhexane hydrobromide, m.p. 177.5—178°, and 3-ethylquinuclidine, b.p. 78—79°/12 mm. [platinichloride, m.p. 220—223° (decomp.); aurichloride, m.p. 178.5—179°; picrate, m.p. 153°; methiodide, m.p. 55°; picrolonate, m.p. 187—188°]. Attempts to resolve the base by *d*-tartaric acid gave the cryst. dl-3-ethylquinuclidine *H* *d*-tartrate,  $[\alpha]_D +14.3^\circ \pm 2^\circ$  in  $\text{H}_2\text{O}$ . Attempted resolution with the aid of *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonic acid leads to an apparently homogeneous salt with m.p. 188—188.5°,  $[\alpha]_D +76.0^\circ \pm 0.5^\circ$  in  $\text{H}_2\text{O}$ , whereas the salt of the homogeneous (+)-base has m.p. 188—189°,  $[\alpha]_D +87.1^\circ \pm 2.0^\circ$  in  $\text{H}_2\text{O}$ ; this appears to be a case of partial racemism.  $\text{OPh}\cdot\text{CH}_2\cdot\text{CHO}$  and  $\text{MgEtBr}$  yield  $\alpha$ -phenoxybutan- $\beta$ -ol, b.p. 134°/20 mm., m.p. 28.5°, converted by  $\text{PBr}_3$  and  $\text{C}_5\text{H}_5\text{N}$  into  $\beta$ -bromo- $\alpha$ -phenoxybutane, b.p. 134—137°/23 mm., which with  $\text{CHNa}(\text{CO}_2\text{Et})_2$  affords *Et*<sub>2</sub>  $\beta$ -phenoxyethylbutane- $\alpha\alpha$ -dicarboxylate, b.p. 220°/15 mm., hydrolysed to the acid, m.p. 114—115°.

IV.  $(\text{CH}_2\cdot\text{OH})_2$ , Na, and *EtI* give  $\text{OEt}\cdot[\text{CH}_2]_5\cdot\text{OH}$ , b.p. 98°/14 mm., converted into  $\text{OEt}\cdot[\text{CH}_2]_5\cdot\text{Br}$ , which with  $\text{CHNa}(\text{CO}_2\text{Et})_2$  in abs. EtOH yields *Et*<sub>2</sub>  $\zeta$ -ethoxyhexane- $\alpha\alpha$ -dicarboxylate, b.p. 165—167°/15 mm. This is converted by  $\text{OEt}\cdot[\text{CH}_2]_5\cdot\text{Br}$  and Na in abs. EtOH into *Et*<sub>2</sub>  $\alpha\lambda$ -diethoxyundecane- $\zeta\zeta$ -dicarboxylate, b.p. 180°/3 mm., hydrolysed and decarboxylated to  $\alpha\lambda$ -diethoxyundecane- $\zeta$ -carboxylic acid, b.p. 180—183°/0.6 mm., which affords  $\zeta$ -amino- $\alpha\lambda$ -diethoxyundecane, b.p. 178°/13 mm. The corresponding hydrobromide is transformed by 68% *HBr* at 100° followed by 0.1*N*-*NaOH* at 50° into dicyclo-[0:5:5]-aza-1-dodecane, b.p. 107—108°/16 mm. (picrate, m.p. 136°; picrolonate, m.p. 181°; methiodide, m.p. 233°).

V. *Et* quinuclidine-2-carboxylate (V), b.p. 122—123°/12 mm., converted by boiling 10% *HCl* into the hydrochloride, m.p. >335°, of the acid, is reduced by Na and abs. EtOH to 2-quinuclidylcarbinol, b.p. 118—120°/14 mm. (picrate, m.p. 230—231°; hydrobromide, m.p. 308°; benzoate hydrochloride, m.p. 245.5—246.5°). *OH* of this compound is very unreactive and is not replaced by *Br* by treatment with 69% *HBr* at 100°. With  $\text{SOCl}_2$  in boiling  $\text{CHCl}_3$ , 2-chloromethylquinuclidine hydrochloride, m.p. 234—235° (corresponding picrate, m.p. 194—195°), results; this could not be dehalogenated by *Zn*-*HCl* or by catalytic reduction.  $\text{MgPhBr}$  and (V) afford diphenyl-2-quinuclidylcarbinol, m.p. 265° (closed capillary) (picrate, m.p. 253—254°), which reacts very sluggishly. H. W.

**Pyrone and related compounds. III. Action of bases on 2:6-dihydroxypyrone.** R. Kaushal (*J. Indian Chem. Soc.*, 1943, 20, 127—130).—2:6-Dihydroxy-1:4-pyrone (I) with  $\text{NH}_2\text{Ph}$  (1 mol.) in  $\text{CHCl}_3$  at room temp. yields acetone- $\alpha\gamma$ -dicarboxylic acid monoanilide, m.p. 120—121°, with excess of  $\text{NH}_2\text{Ph}$  at the b.p. (excess being removed with *HCl*) yields the dianilide, m.p. 157°, and with  $\text{NH}_2\text{Ph}$  and  $\text{ZnCl}_2$  at the b.p. yields 2:6-dihydroxy-1-phenyl-4-pyridone, m.p. 252° (darkens at 230°) (nitrophenylhydrazones, m.p. 184—185°; diacetate, m.p. 190°).  $\text{NH}_4\text{OAc}$  and (I) at 0° yield an oxonium compound,  $\text{C}_5\text{H}_7\text{O}_4\text{N}\cdot\text{H}_2\text{O}$ , m.p. 210°, which gives a violet colour with  $\text{FeCl}_3$ , evolves  $\text{NH}_3$  on heating, yields with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  the monoxime, m.p. 180° (decomp.), and with  $\text{Ac}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  the diacetate, m.p. 160°, of (I) [also obtained from (I) and  $\text{AcCl}$  (trace of  $\text{H}_2\text{SO}_4$ )].  $\text{C}_5\text{H}_5\text{N}$  and piperidine with (I) at 0° yield oxonium compounds, m.p. 152° and 139—140° respectively, which give a violet colour with  $\text{FeCl}_3$  and decompose on warming. A. Li.

**Hydroxypyridines.**—See B., 1943, II, 212.

**Pyridine derivatives.**—See B., 1943, II, 245.

**Synthesis of a pyridine analogue of hydnocarpic acid and of a lower homologue.** F. Brody and M. T. Bogert (*J. Amer. Chem. Soc.*, 1943, 65, 1075—1080).— $\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_8\cdot\text{OH}$  (prep. from  $\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{Et}$  by  $\text{Na}\cdot\text{Bu}^\text{OH}$ ; 77—82% yield) with, best,  $\text{SOCl}_2\cdot\text{C}_6\text{H}_5\text{N}$  at <0° and then 130—140° gives the chloride (83%), b.p. 113—115°/2 mm., which with 2-methylpyridine and commercial  $\text{NaNH}_2$  at 100° or in boiling  $\text{C}_6\text{H}_6$  gives 2- $\Delta^{\lambda}$ -n-dodecenylpyridine (I) (53%), b.p. 158—159°/4 mm. [picrate, m.p. 46—46.5° (46—47°)]. Use of pure  $\text{NaNH}_2$  and a trace of  $\text{Fe}(\text{NO}_2)_3\cdot 6\text{H}_2\text{O}$  in  $\text{NH}_3$ , later at 100°, gives 2- $\Delta^{\lambda}$ -n-dodecenylpyridine (II) (67%), b.p. 152—153°/4 mm. (picrate, m.p. 64.5—65.5°).  $\text{H}_2$ -Pd-black reduces (I) or (II) to 2-n-dodecylpyridine (90%), an oil (picrate, m.p. 64.5—65.5°). With  $\text{AgOBz}$  and then I in  $\text{C}_6\text{H}_6$ , (I) and (II) give 2- $\lambda\mu$ -, m.p. 71.5—72°, and 2- $\kappa\lambda$ -dihydroxy-n-dodecylpyridine, m.p. 87—

87.5°, respectively.  $\text{KMnO}_4$  oxidises (I) in  $\text{COMe}_2$  at <35° to  $\kappa$ -2-pyridyl-n-undecoic acid (III), m.p. 68.5—69.5° [picrate, m.p. 79—79.5°, prepared in  $\text{Et}_2\text{O}$ ; *Et* ester picrate, m.p. 69—70°, formed in EtOH; hydrochloride; Na salt; amide (IV), m.p. 96.5—97.5° (picrate, m.p. 112.5—113°)]. (IV) yields similarly  $\iota$ -2-pyridyl-n-undecoic acid, m.p. 55.5—56.5° (picrate, m.p. 82.5—83°), the chloride hydrochloride of which yields the oily diazomethyl ketone and thence (IV).  $\text{H}_2$ -Raney Ni reduces (III) in cyclohexane at 180°/1700 lb. to  $\kappa$ -2-piperidyl-n-undecoic acid, m.p. 158.5—160° (picrate, m.p. 92.5—93.5°). R. S. C.

**Synthesis of 5-methoxyisatin.** E. Ferber and G. Schmolke (*J. pr. Chem.*, 1940, [ii], 155, 234—240).— $\text{CS}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}\cdot p)_2$ , m.p. 188°, and aq.  $\text{KCN}\cdot\text{PbCO}_3\cdot\text{EtOH}$  at 50—60° give *C*-cyano-*NN'*-di-*p*-anisylamidine,  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}(\text{CN})\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}\cdot p$ , m.p. 157°, converted (35%  $\text{NH}_3$  saturated with  $\text{H}_2\text{S}$ ) at 45° into the *C*-thiocarbonyl compound, m.p. 147° (decomp.), which with conc.  $\text{H}_2\text{SO}_4$  at 65—75°, followed by boiling with dil. mineral acid, yields 5-methoxyisatin, m.p. 201°. A. T. P.

**Alkoxy exchange by  $\gamma$ -alkoxyquinoline derivatives in alcoholic alkali.** B. Berinzaghi, V. Deulofeu, R. Labriola, and A. Muruzabal (*J. Amer. Chem. Soc.*, 1943, 65, 1357—1359).—The 4-OR of skimmianine (I),  $\gamma$ -fagarine (II) (A., 1943, II, 113), and their analogues is labile, being converted into OR' by  $\text{KOH}\cdot\text{R}'\text{OH}$ . Possible reaction mechanisms are discussed. Boiling 10%  $\text{KOH}\cdot\text{EtOH}$  converts (I) into the 4-OEt-analogue (III),  $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}$ , m.p. 138° (picrate, m.p. 194°), which with *MeI* at 100—110° gives isoskimmianine, with  $\text{KMnO}_4\cdot\text{COMe}_2$  gives the 4-OEt-analogues, m.p. 212° (phenylhydrazones, m.p. 178.5°) and 225°, of skimmianal and skimmianic acid, respectively, and with boiling 30% *HCl* gives 2:4-dihydroxy-7:8-dimethoxyquinoline. 5%  $\text{KOH}\cdot\text{Pr}^\text{OH}$  gives similarly the 4-OPr-analogue (IV), m.p. 95° (picrate, m.p. 179—180°), of (I). 5%  $\text{KOH}\cdot\text{MeOH}$  at 100° regenerates (I) from (III) or (IV). Similarly, (II) yields the 4-OEt-analogues, (V) m.p. 143° [picrate, m.p. 161°; with 10%  $\text{KOH}\cdot\text{MeOH}$  at 90—100° regenerates (II)], 192—193° (phenylhydrazones, m.p. 185—186°), and 210—211°, of (II),  $\gamma$ -fagaraldehyde, and  $\gamma$ -fagaric acid, respectively. 30% *HCl* hydrolyses (V) to 2:4-dihydroxy-7- or -8-methoxyquinoline. R. S. C.

**Quinolines.**—See B., 1943, III, 160.

**Synthesis of 1-substituted aminobenzo(f)quinolines.** A. C. Mueller and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1943, 65, 1017—1018).—Adding *Et*<sub>2</sub>  $\alpha$ -2-naphthylaminosuccinate (I) (prep. from  $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$  and  $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  by conc.  $\text{H}_2\text{SO}_4$ ; 41% yield), m.p. 66—67°, to mineral oil at 230° gives *Et* 1-hydroxybenzo(f)quinoline-3-carboxylate [4-hydroxy-5:6-benzquinoline-2-carboxylate] (65%), m.p. 215—217°, hydrolysed by boiling 5% *NaOH* to the acid, m.p. 302° (loss of  $\text{CO}_2$ ). Decarboxylation at the m.p. gives 4-hydroxy-, m.p. 286—288°, converted by boiling  $\text{POCl}_3$  into 4-chloro-5:6-benzquinoline, m.p. 62—63° (lit. 67°), which with the appropriate amine at the b.p. gives 4-morpholino-, m.p. 146—148°, 4-piperidino-, m.p. 138—140°, 4- $\gamma$ -morpholino-n-propylamino-, +2 $\text{H}_2\text{O}$ , m.p. 75—76°, and 1- $\gamma$ -diethylamino-n-propylamino-, m.p. 59—60°, -5:6-benzquinoline.  $\text{H}_2$ -Raney Ni reduces (I) in EtOH at 80°/500 lb. to *Et*<sub>2</sub>  $\alpha$ -2-naphthylaminosuccinate, m.p. 63—65° (hydrochloride, m.p. 140°; derived acid, m.p. 186°; cf. A., 1892, 860). R. S. C.

**[Derivatives of] dihydroresorcinols.** A. Sonn and H. Schreiber (*J. pr. Chem.*, 1940, [ii], 155, 65—76).—5-isoPropyldihydroresorcinol (I) and  $\text{CH}_2\text{O}$  in warm aq. MeOH give 2:2'-methylene-5:5'-diisopropylbis(dihydroresorcinol) (II) (90%), m.p. 183—184°, converted by boiling  $\text{Ac}_2\text{O}$  into 1:8-diketo-3:6-diisopropyl-1:2:3:4:5:6:7:8-octahydroxanthene (III), m.p. 138—140°, which with  $\text{NH}_3\cdot\text{MeOH}$  at room temp. (not 100°) gives 3-amino-3'-hydroxy-5:5'-diisopropyl-2:2'-methylenebis- $\Delta^2$ -cyclohexene (or the 3-NH<sup>+</sup> form), m.p. 173—175°. In boiling  $\text{Ac}_2\text{O}$  this gives 4:6-diketo-2:8-diisopropyl-1:2:3:4:6:7:8:9-octahydroacridine, fluorescent, m.p. 287—290°, which could not be hydrogenated.  $\text{NET}_2\cdot[\text{CH}_2]_2\cdot\text{NH}_2$ , (III), and  $\text{NaOAc}$  in boiling MeOH give 4:6-diketo-5- $\beta$ -diethylaminoethyl-2:8-diisopropyl-1:2:3:4:6:7:8:9-octahydroacridine, m.p. ~176°, which in acid slowly regenerates (II). *p*- or *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  and (I) in warm MeOH give 2:2'-*p*-, m.p. 182—183°, and *m*-nitrobenzylidene-5:5'-diisopropylbis(dihydroresorcinol), m.p. 153—154°, and thence (boiling  $\text{Ac}_2\text{O}$ ) 1:8-diketo-9-*p*-, m.p. 184—186°, and -9-*m*-nitrophenyl-3:6-diisopropyl-1:2:3:4:6:7:8:9-octahydroxanthene, m.p. 148—150°. 2:2'-*p*-Hydroxybenzylidene-5:5'-diisopropylresorcinol, m.p. 123—125°, is similarly obtained in aq. EtOH at room temp. and gives 1:8-diketo-9-*p*-acetoxyl-, m.p. 132°, and thence (conc. *HCl*-EtOH at 100°) -9-*p*-hydroxyphenyl-3:6-diisopropyl-1:2:3:4:6:7:8:9-octahydroxanthene, m.p. 189—190°. Helicin and (I) in boiling EtOH give an oil, converted by  $\text{Ac}_2\text{O}$  into 1:8-diketo-9- $\alpha$ - $\beta$ -glucosidophenyl-3:6-diisopropyl-1:2:3:4:6:7:8:9-octahydroxanthene tetraacetate, m.p. 105—106°.  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$  and (I) in warm MeOH give 2:2'-cinnamylidene-5:5'-diisopropylbis(dihydroresorcinol), m.p. 163—164°.  $\text{CN}\cdot[\text{CH}_2]_2\cdot\text{CH}(\text{OEt})_2$  and (I) in boiling EtOH-AcOH give a product, m.p. ~133—137°, converted by boiling  $\text{Ac}_2\text{O}$  into 1:8-diketo-9- $\beta$ -cyanoethyl-3:6-diisopropyl-1:2:3:4:6:7:8:9-octahydroxanthene, m.p. 153—155°.  $\text{NET}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2\cdot\text{HCl}$  and (I) in warm MeOH give 2:2'-vinylidene-5:5'-diisopropylbis(dihydroresorcinol), m.p. 110°.

OH·CH<sub>2</sub>·CHO or CH<sub>2</sub>Cl·CHO with (I) in MeOH-H<sub>2</sub>O gives 3-keto-5 : 5'-diisopropyl-2 : 2'-dihydroresorcinyll-1 : 2 : 3 : 4 : 5 : 6-hexahydrobenzofuran (IV), m.p. 208—210°. o-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO, (I), and KOH in boiling aq. MeOH give 4-keto-2-isopropyl-1 : 2 : 3 : 4-tetrahydroacridine, m.p. indefinite (picrate, m.p. 193—194°). (II) and its analogues and (IV) are monoenolic forms, since they are sol. in NaOH. R. S. C.

**Polarographically controlled syntheses, with reference to organic chemistry.** J. J. Lingane, C. G. Swain, and M. Fields (*J. Amer. Chem. Soc.*, 1943, 65, 1348—1353).—The use of the polarograph as a control in electrolytic syntheses is suggested, and applied to the reduction of 9-o-iodophenylacridine to 9-o-iodophenyl- and 9-phenyl-dihydroacridine. Almost quant. yields of high purity were obtained. W. R. A.

**Preparation and therapeutic properties of certain acridine derivatives.** IV. 5-Methylacridines, further 5-styrylacridines, and their quaternary salts. W. Sharp, M. M. J. Sutherland, F. J. Wilson, and (in part) C. H. Browning and K. M. Calver (*J.C.S.*, 1943, 344—347; cf. A., 1943, II, 105).—3-Nitro- is reduced (SnCl<sub>2</sub> + HCl) to 3-amino-5-methylacridine, m.p. ~200° (decomp.), the Ac derivative, decomp. ~260° (does not melt at 360°), of which with p-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>Me at 145° yields its metho-p-toluenesulphonate, m.p. 226°, converted by pptn. with aq. NH<sub>3</sub>, boiling the base with conc. HCl, and the resulting iodide with AgCl into 3-amino-5-methylacridine methochloride, m.p. >200° (decomp.). 5 : 2 : 1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Cl·COMe, p-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NHAc, and anhyd. K<sub>2</sub>CO<sub>3</sub> at 125° yield 4-nitro-4'-acetamido-2-acetyldiphenylamine, m.p. 207° (reddens at ~120°), cyclised by AcOH-conc. H<sub>2</sub>SO<sub>4</sub> at 125° to 3-nitro-7-amino-, decomp. ~270° (does not melt at 380°) [Ac derivative, darkens ~280° (does not melt at 360°)], reduced (anhyd. SnCl<sub>2</sub>) to 3 : 7-diamino-5-methylacridine (I), sinters at ~200° (decomp.), the Ac<sub>2</sub> derivative, m.p. <360°, of which is converted via the metho-p-toluenesulphonate into 3 : 7-diamino-5-methylacridine methochloride, decomp. ~200°. Similarly 4-nitro-2-acetyl-4'-methyldiphenylamine, m.p. 132°, yields 3-nitro-, decomp. ~235° (does not melt at 360°), and 3-amino-5 : 7-dimethylacridine, decomp. ~170° [Ac derivative, decomp. ~250° (does not melt at 360°); methochloride, decomp. >200°]. 4-Nitro-3-acetamido-2-acetyldiphenylamine (prep. as above from m-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NHAc) has m.p. 229°. 3-Nitro-5-methylacridine with o- and m-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO alone at 100° yields respectively α-(o-, decomp. 170° (does not melt at 360°), and α-(m-nitrophenyl)-β-5-(3-nitroacridyl)ethanol, decomp. 175°, but with p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO and Ac<sub>2</sub>O at 130° gives 3-nitro-5-p-nitro-, darkens >250° (does not melt at 360°), converted as above into 3-amino-5-p-amino-styrylacridine, decomp. >200° (Ac<sub>2</sub> derivative, m.p. <360°; methochloride, decomp. ~250°). Similarly 3-nitro-5 : 7-dimethyl- yields 3-nitro-5-p-nitro-, m.p. <360°, and 3-amino-5-p-amino-styryl-7-methyl-, decomp. ~200° (Ac<sub>2</sub> derivative, m.p. <360°; methochloride, decomp. >250°), and 3-nitro-7-acetamido-5-methyl- yields 3-nitro-7-acetamido-5-p-nitro-, m.p. <360° (darkens >250°), and 3 : 7-diamino-5-p-amino-styryl-acridine, decomp. ~180° (Ac<sub>3</sub> derivative, m.p. <360°; methochloride, decomp. ~200°). Therapeutic properties of these and other acridine derivatives are recorded. (I) and 3 : 6(or 3 : 8)-diamino-5-methylacridine show antiseptic properties, but 5-aminostyrylacridines do not. The methochlorides have enhanced antiseptic action (especially those of amino-5-amino-styrylacridines), and in some cases trypanocidal action. A. Li.

**Chemotherapy of malaria.** S. J. Das-Gupta (*J. Indian Chem. Soc.*, 1943, 20, 137—138).—2-Chloro-7-methoxy-, m.p. 225°, and 7-methoxy-5-(β-diethylaminoethyl)-, m.p. 209—210° (from the thiolacridine and Br·[CH<sub>2</sub>]<sub>2</sub>·NEt<sub>2</sub> in PhOH containing NaOH at 100—110°), and 2-chloro-7-methoxy-, m.p. 195—197°, and 7-methoxy-5-(γ-diethylaminopropyl)-thiolacridine, m.p. 180—181° (similar prep.), are strongly antiseptic against paramecia. A. Li.

**Pyrroles and pyrromethenes.**—See B., 1943, II, 313.

**Direct replacement of oxygen in hydantoins and barbiturates by sulphur.** H. R. Henze and P. E. Smith (*J. Amer. Chem. Soc.*, 1943, 65, 1090—1092).—The appropriate hydantoins and P<sub>2</sub>S<sub>5</sub> in boiling tetrahydronaphthalene give 5 : 5-dimethyl- (I) (30%), m.p. 147.5—148°, 5 : 5-diphenyl- (18%), m.p. 260—261° (decomp.), and, better in decahydronaphthalene, 5-phenyl-5-methyl- (61%), m.p. 176.5—177°, and 5-phenyl-5-ethyl-thiohydantoin (55%), m.p. 174.5—175°. Barbitol and phenobarbitol give similarly 5 : 5-diethyl- (II) (56%), m.p. 196.5—197°, and 5-phenyl-5-ethyl-2 : 4 : 6-trithiobarbituric acid (22%), m.p. 175—177°, respectively. Boiling 5% NaOH hydrolyses (II) to CEt<sub>2</sub>(CO·NH<sub>2</sub>)<sub>2</sub> (proof of structure). M.p. are corr. None of the products has analgesic or anticonvulsant activity, and only (I) and (II) are hypnotic. R. S. C.

**Stimulation of formation of additive compounds between bases and phenols.**—See A., 1943, I, 259.

**Action of phenylcarbimide on 4-hydroxymethylantipyrine.** P. Duquenois and H. Amal (*Rev. Fac. Sci. Istanbul*, 1942, 7, 1—5).—PhNCO and 4-hydroxymethylantipyrine (I) give 1-phenyl-2 : 3-dimethyl-4-anilinoformylmethylpyrazolone-5-anil (II), m.p. 271.5° (yellow at ~265°), and CO<sub>2</sub>. (II) is hydrolysed by boiling dil. H<sub>2</sub>SO<sub>4</sub>

to CO<sub>2</sub> and NH<sub>2</sub>Ph. An analogous compound is not produced from (I) and PhNCS. H. W.

**Action of phosphorus pentachloride and thionyl chloride on anti-pyrene-4-carboxylic acid.** P. Duquenois and H. Amal (*Rev. Fac. Sci. Istanbul*, 1942, 7, 6—12).—Antipyrine-4-carboxylic acid (I) and SOCl<sub>2</sub> in dry C<sub>6</sub>H<sub>6</sub> at 80—90° give 5-chloro-1-phenyl-3-methylpyrazole-4-carboxylic acid (II), m.p. 227°, partly sublimes at 170—180°. With PCl<sub>5</sub>, directly or in presence of light petroleum, (I) gives (II) and the corresponding chloride (III), m.p. 74°, also obtained from the Ca salt and PCl<sub>5</sub> in presence of CHCl<sub>3</sub>. With a large excess of the requisite alcohol (III) gives Me, m.p. 74° and Et, m.p. 68°, 5-chloro-1-phenyl-3-methylpyrazole-4-carboxylate. H. W.

**Barbituric acids.**—See B., 1943, II, 246.

**Pyrimidines.** CLXXVIII. Chlorination of 2 : 4-diketotetrahydropyrimidines by action of a mixture of hydrogen peroxide and hydrochloric acid. CLXXIX. Reaction of hydrochloric acid with 5 : 5-dichloro-6-methylhydrouracil. T. B. Johnson (*J. Amer. Chem. Soc.*, 1943, 65, 1218—1219, 1220—1222).—CLXXVIII. 30% H<sub>2</sub>O<sub>2</sub> + conc. HCl at room temp. effects nearly quant. chlorination of 2 : 6-diketotetrahydropyrimidines. 5 : 5-Dichloro-4-hydroxyhydrouracil is obtained from uracil, 6-hydroxy-2-ethylthiopyrimidine, cytosine, 5-iodouracil, or, with CO<sub>2</sub>, uracil-5-carboxylic acid. Thymine gives 5-chloro-4-hydroxy-5-methylhydrouracil, m.p. 202—203°. 4-Methyluracil gives 5 : 5-dichloro-4-hydroxy-4-methylhydrouracil. 5-Bromo- and 5-nitro-uracil give 5-chloro-5-nitro- and 5-chloro-5-nitro-4-hydroxyhydrouracil, respectively. isoCytosine gives 5 : 5-dichloro-2-amino-4-hydroxy-6-ketohexahydropyrimidine hydrochloride. Orotic acid gives 5-chlorouracil-4-carboxylic acid, m.p. >300°. Hydrouracil does not react.

CLXXIX. 5 : 5-Dibromo-4-hydroxy-4-methylhydrouracil in boiling conc. HCl or Ac<sub>2</sub>O gives 5-bromo-6-methyluracil, but 5 : 5-dichloro-4-hydroxy-4-methylhydrouracil gives the ether, (NH<CO·CCl>CMe)<sub>2</sub>O, m.p. 270—275° (decomp.) (mol. wt. in boiling C<sub>6</sub>H<sub>6</sub>). (I) is converted by SnCl<sub>2</sub>-dil. HCl at 100° or conc. aq. NH<sub>3</sub> at room temp. (1 week) into 5-chloro-6-methyluracil and by boiling HI (d 1.5) into 6-methyluracil. R. S. C.

**Pyrimidines.**—See B., 1943, III, 193.

**Reactions of amidines with derivatives of malonic acid.** G. W. Kenner, B. Lythgoe, A. R. Todd, and A. Topham (*J.C.S.*, 1943, 388—390).—In presence of NaOEt in EtOH, CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> with NH·CH·NH<sub>2</sub>·HCl (room temp.) yields 4 : 6-dihydroxy-, decomp. >230°, and with α-furylamidine hydrochloride (I) (at the b.p.) yields 4 : 6-dihydroxy-2-α-furyl-pyrimidine, decomp. >290°. With CH<sub>2</sub>(CN)<sub>2</sub>, NH·CMe·NH<sub>2</sub>·HCl and NH·CPh·NH<sub>2</sub>·HCl (room temp.) yield 4-amino-5-cyano-2 : 6-dimethyl-, m.p. 218°, and -2 : 6-diphenylpyrimidine, m.p. 211°, respectively, whilst (I) at the b.p. yields β-(2'-furyl)-β-aminomethylenemalononitrile, m.p. 182°, which further reacts with (I) to give 4-amino-5-cyano-3 : 6-di-2'-furylpyrimidine, m.p. 245—246°. NH·CH·NH<sub>2</sub>·HCl with NH<sub>2</sub>·CH·C(CN)<sub>2</sub> at room temp. yields 4-amino-5-cyanopyrimidine (II), and with CN·CH<sub>2</sub>·CO<sub>2</sub>Et gives, according to conditions, NH<sub>2</sub>·CH·C(CN)·CO<sub>2</sub>Et (converted by MeCS·NH<sub>2</sub> and NaOEt in EtOH into 4-amino-2-methylpyrimidine-5-carboxylate), Et methylenebiscyanoacetate (III), or a compound, C<sub>6</sub>H<sub>5</sub>O<sub>3</sub>N<sub>3</sub> (? 4-amino-6-hydroxy-3-carbethoxy-5-cyanopyridine), m.p. 280—281° (decomp.). With CN·CH<sub>2</sub>·CO<sub>2</sub>Et, NH·CPh·NH<sub>2</sub>·HCl yields β-amino-α-cyano-β-phenylacrylate (IV) and 4-amino-6-hydroxy-2-phenylpyrimidine, whilst NH·CPh·OEt gives only (IV) (small yield). NH·CH·NH<sub>2</sub>·HCl and CH<sub>2</sub>Ac·CO<sub>2</sub>Et yield a compound, C<sub>11</sub>H<sub>15</sub>O<sub>5</sub>N (? CO<sub>2</sub>Et·Cac·CH·NH·CO·CH<sub>2</sub>Ac), m.p. 78—79° [which could not be prepared from CH<sub>2</sub>Ac·CO<sub>2</sub>Et and NH<sub>2</sub>·CH·C(CN)·CO<sub>2</sub>Et]. NH·CH·OEt·HCl yields with CH<sub>2</sub>(CN)<sub>2</sub>, (II), with CN·CH<sub>2</sub>·CO<sub>2</sub>Et (without NaOEt), NH<sub>2</sub>·CH·C(CN)·CO<sub>2</sub>Et, or (with NaOEt) a small amount of the latter with (III), and with CH<sub>2</sub>Ac·CO<sub>2</sub>Et, (III) and a small amount of solid, m.p. 201°. A. Li.

**Preparation and reactions of benziminazole-2-carboxylic acid and 2-benziminazolylacetic acid.** R. A. B. Copeland and A. R. Day (*J. Amer. Chem. Soc.*, 1943, 65, 1072—1075).—2-Hydroxymethylbenziminazole [prep. from o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> and OH·CH<sub>2</sub>·CO<sub>2</sub>H], m.p. 171—172°, and KMnO<sub>4</sub> give benziminazole-2-carboxylic acid (I) (71%), +2H<sub>2</sub>O, m.p. 169—171° (loss of CO<sub>2</sub>), which in boiling SOCl<sub>2</sub> gives 3 : 6-diketodi(benziminazole-1' : 2'-)1' : 2-4 : 5-tetrahydropyrazine (II), m.p. >300°. In boiling conc. HCl or N-NaOH, (II) gives (I), in hot 10% HCl-EtOH gives the Et ester (III), m.p. 212.7—213.7° or 228—230° (block), of (I), and in NaOEt-EtOH gives the Na derivative of (III), which in 1 : 1 AcOH-H<sub>2</sub>O gives (III) but in warm H<sub>2</sub>O gives (I). In NaOMe-MeOH, (II) gives the Me ester, m.p. 187.3°, of (I). With NH<sub>3</sub> or the appropriate amine in hot H<sub>2</sub>O, (II) gives benziminazole-2-carboxylamide, m.p. >300°, -methyl-, m.p. 246.5°, -ethyl-, m.p. 210—211°, -β-hydroxyethyl-, m.p. 219—220°, -β-methoxyethyl-, m.p. 138°, -n-butyl-, m.p. 180.5—181.5°, -benzyl-, m.p. 172.4°, -cyclohexyl-, m.p. 269.5°, -dimethyl-, m.p. 223—224°, -diethyl-, m.p. 124.5°, add -di-n-butyl-amide, m.p. 101.2°, and -morpholide, m.p. 181.2°. o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> and CN·CH<sub>2</sub>·CO<sub>2</sub>Et at 165—200° (63%) or

180° (70%) give 2-cyanomethylbenziminazole, m.p. 209.7—210.7°, hydrolysed by boiling 50%  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$ -aq. EtOH to 2-benziminazolylacetic acid, m.p. 116° [loses  $\text{CO}_2$ , resolidifies, remelts at 176° (2-methylbenziminazole)], or by 9%  $\text{HCl}$ -EtOH to the *Et* ester, m.p. 128.5—129.5°, thereof and thence (aq.  $\text{NH}_3$ ) giving the *amide*, m.p. 244—247° (decomp.), -methyl-, m.p. 214—216.5° (decomp.), -*n*-butyl-, m.p. 209.5—212.5° (decomp.), and - $\beta$ -methoxyethyl-*amide*, m.p. 183.5—185° (decomp.). M.p. are corr. R. S. C.

Quinoxaline formation and the ortho-effect. R. C. Eason, C. H. McKeever, N. Rabjohn, and H. W. Gray (*J. Amer. Chem. Soc.*, 1943, 65, 1023—1029).—6 : 2 : 4 : 1- $\text{OMe}-\text{C}_6\text{H}_4\text{Me}_2\text{COMe}$  (prep. from 1 : 3 : 5- $\text{C}_6\text{H}_3\text{Me}_2\text{OMe}$  by  $\text{Ac}_2\text{O}-\text{AlCl}_3$  in boiling  $\text{CS}_2$ ) with  $\text{SeO}_2$  and a little  $\text{H}_2\text{O}$  in boiling dioxan gives 6-methoxy-2 : 4-dimethylphenylglyoxal, b.p. 90—120°/4 mm., which, in contrast to 2 : 4 : 6 : 1- $\text{C}_6\text{H}_3\text{Me}_2\text{CO}-\text{CHO}$  (I) (A., 1939, II, 162), with  $\alpha\text{-C}_6\text{H}_4(\text{NH}_2)_2$  in boiling  $\text{AcOH}$  gives 2-6'-methoxy-2' : 4'-dimethylphenylglyoxaline, m.p. 83.5—84°. 2 : 6 : 1-( $\text{OMe}$ ) $_2\text{C}_6\text{H}_3\text{CO}-\text{CHO}$ , b.p. 115—117°/5 mm., gives 2-2' : 6'-dimethylphenylglyoxaline, m.p. 95.5—96.5°, and, when shaken with 30%  $\text{NaOH}$ , gives 2 : 6-dimethoxymandelic acid, m.p. 146—147°. 3 : 5 : 2 : 4 : 6 : 1-( $\text{NO}_2$ ) $_2\text{C}_6\text{H}_2\text{CO}-\text{CHO}$  (prep. from the  $\text{COMe}$  derivative by  $\text{SeO}_2$  in boiling aq. dioxan), softens at 116°, m.p. 122—125°, gives 2-3' : 5'-dinitromesityl-glyoxaline, m.p. 197.5—198°, the hindrance of (I) being overcome by chelation of the  $\text{NO}_2$  and  $\text{Me}$ . R. S. C.

Niementowski reaction. Use of methyl anthranilate or isatoic anhydride with substituted amides or amidines in the formation of 3-substituted 4-keto-3 : 4-dihydroquinazolines. Course of the reaction. J. F. Meyer and E. C. Wagner (*J. Org. Chem.*, 1943, 8, 239—252).—In the prep. of 4-keto-3 : 4-dihydroquinazolines the yields may be decreased by the formation of stable quinazolone anthranilates in the reaction mixture, thus making part of the anthranilic acid (I) unavailable for the synthesis. This behaviour, observed in the prep. of 3-phenyl-3 : 4-dihydroquinazol-4-one (II), seems not to be general and its interference can be minimised by the use of >1 equiv. of (I). The anthranilate, m.p. 132.2° (corr.), benzoate, m.p. 131—132°, salicylate, m.p. 168—169°, phenylacetate, m.p. 113—114°, and formate, m.p. 119—120°, of (II), the anthranilate, m.p. 111—113°, and of 3-m-tolyl-3 : 4-dihydroquinazol-4-one, and the anthranilate, m.p. 119—121°, of 3-p-tolyl-3 : 4-dihydroquinazol-4-one are reported.  $\alpha\text{-NH}_2\text{-C}_6\text{H}_4\text{CO}_2\text{Me}$  (III) can replace (I) in the Niementowski reaction, its use permitting (and requiring) higher reaction temp. than can be maintained with (I). With respect to yield and applicability this modification of the Niementowski reaction is without advantage. Diaryl-formamidines (IV) or -acetamidines can be used instead of amides in the Niementowski reaction with either (I) or (III). Yields are good when (III) and (IV) react. This reaction shows a functional analogy between amides and amidines considered respectively as aquo-ammono-acids and ammono-acids. A new quinazolone synthesis from isatoic anhydride and diarylamidines is described, high yields resulting from the use of diarylformamidines. The synthesis follows two divergent courses, each leading to the same product. By use of acetamidines only one reaction course leading to the quinazolone is open (the other terminating with the formation of the anthranilamide), with the result that yields are relatively lower. (III) and  $\text{NH}_2\text{Ac}$  afford  $\alpha\text{-NHAc-C}_6\text{H}_4\text{CO}_2\text{Me}$ , 2-methyl-3 : 4-dihydroquinazol-4-one, and traces of  $\text{NH}_3$ . This result indicates the sequence of reactions by which (III) and amides yield quinazolones and provides collateral experimental support for the two assumed steps in the reaction course proposed by Bogert *et al.* for the Niementowski synthesis. H. W.

Constitution of 1-phenyl-*d*-fructosone.—See A., 1943, II, 294.

Synthesis of purine nucleosides. I. Model experiments on synthesis of 9-alkylpurines. J. Baddiley, B. Lythgoe, D. McNeil, and A. R. Todd. II. Synthesis of adenine. J. Baddiley, B. Lythgoe, and A. R. Todd (*J.C.S.*, 1943, 383—386, 386—387).—I. With aq.  $\text{HCS}_2\text{Na}$ , 4 : 5-diamino-6-hydroxy-2-methyl-, 4 : 5 : 6-triamino-2-methylthiol-, m.p. 182° (prep. by reduction [( $\text{NH}_4$ ) $_2\text{S}$ ] of the product from 4 : 6-diamino-2-methylthiopyrimidine and  $\text{HNO}_3$ ), 4 : 6-diamino-2-methyl- (I), m.p. 294—295° (sealed tube) (picrate, decomp. >250°), 5-amino-4-methylamino-2-hydroxy-6-methyl-, and the product of nitrosation and reduction (as above) of 6-amino-4-methylamino-2-methylthiol-pyrimidine, m.p. 143—144° (from the 4-Cl-compound and aq.  $\text{NH}_3\text{Me}$  at 100° in a sealed tube), yield 5-thioformyl derivatives, m.p. >260° (decomp. without melting), 235° (decomp., rapid hearing), (no definite m.p.), <300°, and 185—186° (evolution of  $\text{H}_2\text{S}$ ) respectively, which when boiled in  $\text{H}_2\text{O}$  or (better) quinoline or other anhyd. org. solvent yield respectively 6-hydroxy-2-methylpurine, decomp. >360°, 2-methylthioladenine (II), m.p. 290° (decomp.), 2-methyladenine, m.p. <300° (picrate, decomp. >250°), 2-hydroxy-6 : 9-dimethylpurine, m.p. <300°, and 2-methylthiol-9-methyladenine, m.p. 261—262° [also obtained from (II),  $\text{MeI}$ , and  $\text{EtOH}-\text{NaOH}$  at room temp.], deaminated by dil.  $\text{AcOH}$  followed by  $\text{Ba}(\text{NO}_3)_2$  at 60—65° to 6-hydroxy-2-methylthiol-9-methylpurine, m.p. 332° (decomp.). (I) is obtained from 4 : 6-dihydroxy-2-methylpyrimidine by treating with  $\text{POCl}_3$ , heating the resulting  $\text{Cl}_2$ -compound, m.p. 48—49°, with  $\text{MeOH}-\text{NH}_3$  at 130°, and the

4-chloro-6-amino-compound, m.p. 190—191°, so formed with  $\text{MeOH}-\text{NH}_3$  at 200°.

II.  $\text{CH}_3(\text{CN})_2$  with  $\text{NH}_2\text{CH}-\text{NH}_2\text{HCl}$  and  $\text{NaOEt}$  in  $\text{EtOH}$  at room temp. yields 4-amino-5-cyanopyrimidine, m.p. 250° (picrate, m.p. 189°) [also obtained from  $\text{NH}_2\text{CH}_2\text{CH}(\text{CN})_2$ ,  $\text{HCS}-\text{NH}_2$ , and  $\text{NaOEt}$  in boiling  $\text{EtOH}$ ], which with boiling  $\text{Ac}_2\text{O}$  gives acetylformamidomethylenemalononitrile, m.p. 124—125°.  $\text{PhN}_2\text{CH}(\text{CN})_2$ ,  $\text{NH}_2\text{CH}-\text{NH}_2\text{HCl}$ , and  $\text{NaOEt}$  in  $\text{EtOH}$  at room temp., then at the b.p., yield 4 : 6-diamino-5-benzeneazopyrimidine, m.p. 282—286° (decomp.), hydrogenated (Raney Ni) to 4 : 5 : 6-triaminopyrimidine, m.p. 257°, the thioformyl derivative, decomp. >200° (evolution of  $\text{H}_2\text{S}$ ), of which in boiling  $\text{H}_2\text{O}$ ,  $\text{C}_5\text{H}_5\text{N}$ , or quinoline yields adenine.

A. Li.

Wing pigments of butterflies. IX. "Anhydroleucopterin" and "purpurorflavin." H. Wieland, A. Tartter, and R. Purrmann (*Annalen*, 1940, 545, 209—219).—Renewed investigation has shown that "anhydroleucopterin" (A., 1933, 1310) is a deoxyleucopterin (I),  $\text{C}_8\text{H}_5\text{O}_2\text{N}_4$ , and thus an isomere of xanthopterin (II). Its re-oxidation to leucopterin (III) has not been achieved. Reduction of leucopterin chloride is effected with difficulty by  $\text{HI}-\text{AcOH}$  and leads to 6-deoxyleucopterin (IV), which does not give the murexide reaction and in  $\text{N}-\text{Na}_2\text{CO}_3$  shows a more marked fluorescence than (I) in ultra-violet light. (IV) is obtained synthetically by heating 2 : 4 : 5-triaminopyrimidine hydrochloride with  $\text{Na}_2\text{C}_2\text{O}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$  at 260°. It is probable that one of the O of the oxalyl CO groups has been replaced by H in the formation of (I). Fuming  $\text{HI}$  reacts immediately with (I) with separation of I, but the hydro-product is very readily dehydrogenated, even by diluting the solution. Reduction by  $\text{HI}$  is an excellent method of separating (I) from (III). Similarly (II) is immediately reduced by  $\text{HI}$  but the colourless compound is not immediately dehydrogenated when the solution is diluted. The previous distinction (*loc. cit.*) between (III) and iso-leucopterin (V) was based on a supposed difference in behaviour towards 0.1N- $\text{NaOH}$ . The method is now found untrustworthy and examination of the Ba salts shows (V) to be non-existent.  $\psi$ -Leucopterin (*loc. cit.*) is impure (III). 4 : 5-Diamino-2 : 6-dihydroxypyrimidine condenses with alloxan in  $\text{H}_2\text{O}$  at room temp. to 4-amino-purpuric acid,  $\text{CO}-\text{NH}-\text{CO}-\text{C}(\text{NH}_2)=\text{C}(\text{NH})-\text{CO}-\text{NH}-\text{CO}$ , m.p. >270°, which under the influence of acid, alkali, or increased temp. or when kept in solution passes into dialloxazine,  $\text{NH}-\text{CO}-\text{C}(\text{NH})=\text{C}(\text{NH})-\text{CO}-\text{NH}-\text{CO}-\text{NH}-\text{CO}-\text{C}(\text{NH})=\text{C}(\text{NH})-\text{CO}-\text{NH}-\text{CO}$ , m.p. >270°. H. W.

Wing pigments of butterflies. VIII. Pterobilin, the blue pigment from *Pierida* wings. H. Wieland and A. Tartter (*Annalen*, 1940, 545, 197—208; cf. A., 1937, II, 392).—After treatment with  $\text{Et}_2\text{O}$  the wings are extracted with  $\text{H}_2\text{O}$  and the blue chromoprotein is pptd. from the aq. extract by  $(\text{NH}_4)_2\text{SO}_4$ . It is decomposed by dil.  $\text{HCl}$  or more simply by  $\text{MeOH}$  into the protein and pterobilin, m.p. >315°, softens and blackens at 200°, which is thus obtained from the wings of *P. brassicae*, *P. rapae*, *P. napi*, *Gonepteryx rhamni*, *C. rurina*, and *C. statira*, but not from *P. crataegi*. It is converted by  $\text{CH}_3\text{N}_3$  in  $\text{Et}_2\text{O}-\text{EtOAc}$  into the  $\text{Me}_2$  ester, melting at 232—234° to a blue melt which becomes red-violet at ~275° and yellow-brown at 300°. This gives the Gmelin reaction and, in contrast to the esters of biliverdin and uteroverdin, is remarkably stable to conc.  $\text{H}_2\text{SO}_4$  at 100°. It contains 3 active H. The  $\text{Zn}$  salt,  $\text{C}_{25}\text{H}_{34}\text{O}_4\text{N}_4\text{Zn}$ , m.p. >300°, appears from its behaviour towards I to contain 2 vinyl groups. With  $\text{FeCl}_3$  in glacial acetic acid the ester affords ferro-bilin, m.p. >300°. The chemical and physical properties of pterobilin indicate that it is a derivative of the bilitriene group with 4 Me, 2  $\text{C}_6\text{H}_4\text{CO}_2\text{H}$ , and 2  $\text{CH}_2\text{CH}_3$  groups in the  $\beta$ -positions. The arrangement of these substituents must differ from that in bilirubin or biliverdin. H. W.

Constitution of the prosthetic group of cytochrome-c. K. Zeile and H. Meyer (*Z. physiol. Chem.*, 1939, 262, 178—198).—The crude adduct of protoporphyrin (prep. from hamin by  $\text{HBr}-\text{AcOH}$  at 40°) or haematoporphyrin, when melted with *L*-cysteine hydrochloride, exchanges the two Br or OH, respectively, for  $-\text{S}-\text{CH}_2\text{CH}(\text{NH}_2)-\text{CO}_2\text{H}$ , giving dicysteine-protoporphyrin (I), which with  $\text{CH}_3\text{N}_3-\text{MeOH}-\text{Et}_2\text{O}$ -conc.  $\text{HCl}$  (a little) gives the  $\text{Me}_2$  ester (II) (~80% : ~50% obtained by  $\text{HCl}-\text{MeOH}$ ),  $\text{C}_{44}\text{H}_{56}\text{O}_8\text{N}_4\text{S}_2$ , amorphous,  $[\alpha]_{\text{white}}^{17} +27^\circ$  in 0.1%  $\text{HCl}$ . (II) is removed from  $\text{Et}_2\text{O}$  by 0.006%  $\text{HCl}$  and by a citrate buffer having pH 2.97 but not 4.92 (hence purification). (I) is only slightly sol. at the isoelectric point, pH 4, but readily at other pH. Acyl derivatives and urethanes could not be obtained, possibly because (II) is unstable, e.g., to chromatography and keeping in  $\text{Et}_2\text{O}-\text{N}_2$  in the dark. Acidic hydrolysis of cytochrome-c usually gives mixtures because of re-synthesis, but use of ~10<sup>-4</sup>M. solutions in 20%  $\text{H}_2\text{SO}_4$ , neutralisation, adsorption on kaolin, elution by dil. aq.  $\text{NH}_3$ , and esterification ( $\text{HCl}-\text{MeOH}$ ) gives ~67% of an isomere (III),  $-\text{H}_2\text{O}$ ,  $[\alpha]_{\text{white}}^{17} +172^\circ$  in 0.1%  $\text{HCl}$ , of (II). (II) and (III) are indistinguishable in solubility, partition coeff., and absorption spectra (detailed). When Fe is introduced into (II), the haemochromogen spectrum (max. at 550 m $\mu$ ) appears at once. Thus, the  $\text{NH}_2$  of the side-chain is co-ordinated with the Fe.

R. S. C.

**Colouring matters of bile.** W. Siedel (*Angew. Chem.*, 1940, **53**, 397—403).—A review.

**Porphyrin-like products of the reaction of pyrrole with benzaldehyde.** S. Aronoff and M. Calvin (*J. Org. Chem.*, 1943, **8**, 205—223).—The reaction of pyrrole with PhCHO yields six porphyrin-like compounds which may be separated chromatographically. At present they may be distinguished, when separated, by absorption spectra and crystal forms. At least two of these, and possibly all six, are isomeric. The two known isomerides are not interconvertible by means of their Cu complexes or hydrochlorides. Their acid vals. are 13.5 and 19.5 respectively. Various distinguishing properties, including polybasicity, are discussed. A method for the spectroscopic determination of polybasic ionisation const. in a system with > 2 mol. species is presented. The absorption spectra of the Cu salts of the isomerides are given. The nature of the porphyrin nucleus is discussed. The possible structure of these isomerides is presented and a new class of compound, carboporphines, is proposed.

H. W.

**X-Ray crystallography of ætioporphyrin-1.**—See A., 1943, I, 251.

**Di-triazine compounds.**—See B., 1943, II, 213.

**2-Thiol-5 : 5-dimethyloxazoline.**—See B., 1943, II, 231.

**Stereoisomeric forms of additive compounds of alcohols and substituted 7-nitrostilbenes.**—See A., 1943, II, 325.

**Reactions of 4-β-chloroethylmorpholine and rates of reaction of 4-β-chloroethylmorpholine and other halides with sodium propoxide.** S. Malkiel [with J. P. Mason] (*J. Org. Chem.*, 1943, **8**, 199—204).—4-β-Chloroethylmorpholine (I) is transformed by boiling aq. Na<sub>2</sub>SO<sub>3</sub> into Na β-4-morpholinoethylsulphonate, converted by picric acid in EtOH into β-4-morpholinoethylsulphonic acid picrate, m.p. 178.8—182.0°. Gradual addition of (I) to MgPhBr at 100° leads to 4-β-phenylethylmorpholine, b.p. 132—135°/5 mm. (picrate, m.p. 170°). Et<sub>2</sub> β-4-morpholinoethylmalonate, b.p. 168—176°/4 mm., from (I) and CHNa(CO<sub>2</sub>Et)<sub>2</sub> in EtOH, gives a methiodide, m.p. 92.2° (corr.), but does not afford a cryst. picrate, 3 : 5-dinitrobenzoate, p-toluenesulphonate, or quaternary metho-p-toluene-sulphonate. Towards NaOPr<sup>a</sup> (I) is less reactive than CH<sub>2</sub>PhCl but more reactive than Ph·[CH<sub>2</sub>]<sub>2</sub>·Cl and very much more reactive than Bu<sup>a</sup>Cl, OPh·[CH<sub>2</sub>]<sub>2</sub>·Cl, or OEt·[CH<sub>2</sub>]<sub>2</sub>·Cl.

H. W.

**Action of sulphonazides on heterocyclic compounds.** (Miss) B. S. Alamela and K. Ganapathi (*Current Sci.*, 1943, **12**, 119).—The action of p-NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>N<sub>3</sub> on thiazole, 2 : 4-dimethyl- and 2-hydroxy-4-methyl-thiazole, C<sub>5</sub>H<sub>5</sub>N, and glyoxaline does not yield any new compounds.

F. R. G.

**Thiazan-3 : 5-dicarboxylic acid derivatives.**—See B., 1943, II, 212.

**Thiazolines.**—See B., 1943, II, 312.

**Thiazoles. XXVII. Thiazole analogue of hydnocarpic acid.** F. Brody and M. T. Bogert (*J. Amer. Chem. Soc.*, 1943, **65**, 1080—1082; cf. A., 1943, II, 110).—Undecenoyl iodide (prep. from the chloride by NaI in boiling, dry COMe<sub>2</sub>; 91% yield), b.p. 104°/2 mm., CN·CH<sub>2</sub>·CO<sub>2</sub>Et, and K<sub>2</sub>CO<sub>3</sub> at 130—150°/18—20 mm. give Et α-cyano-Δ<sup>1</sup>-tridecenoate (83%), b.p. 142—144°/1 mm., slowly reduced by H<sub>2</sub>S and a little N[(CH<sub>2</sub>)<sub>2</sub>·OH]<sub>3</sub> in EtOH, cold and then at 50°, to Et α-carbethoxy-Δ<sup>1</sup>-tridecenothioamide (66%), m.p. 63.5—64°. With CH<sub>2</sub>Cl·CHO, H<sub>2</sub>O (prep. from the acetal by boiling with anhyd. H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) in C<sub>6</sub>H<sub>6</sub> at ~70°, this gives by condensation, hydrolysis, and decarboxylation, 2-Δ<sup>1</sup>-dodecenylthiazole (63%), b.p. 127°/1 mm. (picrate, m.p. 91—92°), oxidised by KMnO<sub>4</sub> in COMe<sub>2</sub> at <40° to λ-2-thiazolyl-n-undecic acid (70%), m.p. 40—41.5° [picrate, m.p. 100—106° (decomp.)]. 2 : 4-Dimethylthiazole and n-C<sub>6</sub>H<sub>13</sub>·CHO in Ac<sub>2</sub>O at 240—265° give α-4-methyl-2-thiazolyl-Δ<sup>a</sup>-n-octene (picrate, m.p. 73°).

R. S. C.

**Reaction of carbon disulphide with amine sulphides.** E. S. Blake (*J. Amer. Chem. Soc.*, 1943, **65**, 1267—1269).—The products obtained from (NR<sub>2</sub>)<sub>2</sub>S or (NR<sub>2</sub>·CS)<sub>2</sub> by CS<sub>2</sub> depend on the nature of R. Adding bisdimethylamine sulphide, (NMe<sub>2</sub>)<sub>2</sub>S (prep. from NHMe<sub>2</sub> by SCl<sub>2</sub> in Et<sub>2</sub>O at <5°; 54.1% yield) (1 mol.), f.p. 20°, b.p. 33.5—36°/14 mm., with cooling and stirring to CS<sub>2</sub> (excess; 2 mols. required) gives 99.1% of pure (NR<sub>2</sub>·CS)<sub>2</sub> and S (1 atom). Similarly, (NEt<sub>2</sub>)<sub>2</sub>S (prep. as above; 52.2% yield), b.p. 79—80°/14 mm., gives (NEt<sub>2</sub>·CS)<sub>2</sub>, an unidentified gas, and S. Dimorpholine disulphide [prep. from morpholine (I) and S<sub>2</sub>Cl<sub>2</sub> in light petroleum (b.p. 87—98°) at <5°; 85.4% yield], m.p. 124—125°, and a trace of (I) in boiling CS<sub>2</sub> give di-N-γ-oxapentamethylenethiuram trisulphide, (O<CH<sub>2</sub>·CH<sub>2</sub>>N·CS)<sub>2</sub>S<sub>3</sub> (II) (96.2%), m.p. 152—153°, and S; dimorpholine sulphide (prep. as above but by SCl<sub>2</sub>; 42.2% yield), m.p. 125—126°, gives similarly, but more slowly, (II) (94.3%) and only a trace of S. Piperidine sulphide (4 mols.) and CS<sub>2</sub> (8 mols. required) in C<sub>6</sub>H<sub>6</sub> at room temp. give di-N-pentamethylenethiuram hexa- (III) (1 mol.), m.p. 137—138° (lit. 129°), and di-sulphide (IV) (3 mols.), m.p. 137°. Piperidine disulphide (2 mols.) and CS<sub>2</sub> (4 mols. required) give similarly (III) (1) and (IV) (1 mol.). Benzthiazole-2-sulphenylcyclohexylamide (1) and CS<sub>2</sub> (1 mol. required) in Et<sub>2</sub>O give 2-thiolbenzthiazole (V) (93.9%), cyclohexylthiocarb-

imide (VI) (86%), b.p. 97—98°/11—12 mm., 222°/749 mm., and S (1 atom). Benzthiazole-2-sulphenylpiperidide and CS<sub>2</sub> in COMe<sub>2</sub> or, much more slowly, Et<sub>2</sub>O, both at room temp., give di-2-benzthiazolyl disulphide (1) and (V) (1 mol.). Amine sulfoxides do not react with CS<sub>2</sub>.

R. S. C.

**Phenthiazines.**—See B., 1943, II, 310.

**Methylene-blue and other indicators in general acids.**—See A., 1943, I, 257.

**Dimeric and other forms of methylene-blue. Absorption and fluorescence of the monomer.**—See A., 1943, I, 248.

**Aldehyde derivatives of heterocyclic compounds.**—See B., 1943, II, 278.

**Sulphanilamide derivatives possessing heterocyclic rings : sulphanilamidothiodiazoles.** P. C. Guha and D. B. Das Gupta (*Current Sci.*, 1943, **12**, 120).—2 : 5-Diamino-, 2-amino-, 2-amino-5-methyl-, and 2-amino-5-methylthiol-1 : 3 : 4-thiodiazole with p-NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Cl yield the sulphanilacetamido-derivatives, m.p. 250—254°, >300°, 200° (decomp.), and 216—218° respectively, deacetylated to the corresponding sulphanilamides, m.p. 223°, 213—214°, 186—187°, and 198°.

F. R. G.

**Synthesis of sulphanilamide derivatives of mixed sulphides possessing heterocyclic rings.** P. C. Guha and V. M. Dokras (*Current Sci.*, 1943, **12**, 120).—Phenyldithiodiazolonyl disulphide with NH<sub>2</sub>Ph gives the aminophenyl sulphide (p-NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub> derivative, m.p. 222°, the deacetylated compound of which has m.p. 173°) and with p-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NH<sub>2</sub> yields 2-p-sulphonamidoanilinothiol-4-phenylthiazolthione.

F. R. G.

**Pyrazoles.**—See B., 1943, II, 302.

**Cyanine dyes.**—See B., 1943, II, 246, 247, 268.

**Fluorescence of monomethine-cyanine dyes.**—See A., 1943, I, 248.

## VII.—ALKALOIDS.

**Alkaloids of the Lycopodium species. III. Lycopodium annotinum, L.** R. H. F. Manske and L. Marion (*Canad. J. Res.*, 1943, **21**, B, 92—96).—*L. annotinum*, L., contains the lactone base *annotine* (0.84), C<sub>16</sub>H<sub>21</sub>O<sub>3</sub>N, m.p. 232° (perchlorate, m.p. 267°), *obscurine* (0.09), lycopodine (0.07), and (<0.01% each) *alkaloids* L8, C<sub>16</sub>H<sub>25</sub>O<sub>2</sub>N, m.p. 180° [perchlorate, m.p. 318° (decomp.) (bath pre-heated to 300°)], L9, m.p. 122°, probably a mixture of C<sub>16</sub>H<sub>23</sub>ON [perchlorate, m.p. 276° (previous darkening)] and C<sub>20</sub>H<sub>31</sub>O<sub>4</sub>N, m.p. 98° (perchlorate, m.p. 273.5°), L10, C<sub>16</sub>H<sub>27</sub>ON (perchlorate, m.p. 223°), L11, C<sub>16</sub>H<sub>21</sub>O<sub>3</sub>N, m.p. 176° (perchlorate, m.p. 239°), and L12, C<sub>18</sub>H<sub>25</sub>O<sub>3</sub>N, m.p. 119° (perchlorate, m.p. 244°). All m.p. are corr.

A. Li.

**Cinchona alkaloids in pneumonia. XI. Ethers of apocupreine.** R. S. Tipson, (Miss) M. A. Clapp, and L. H. Cretcher (*J. Amer. Chem. Soc.*, 1943, **65**, 1092—1094; cf. A., 1942, II, 336).—β-α'-, m.p. 34—35°, and β-β'-phenylethoxyethyl p-toluenesulphonate, m.p. 39—40°, are prepared. β-γ-isoPropylideneglyceryl α-p-toluenesulphonate, m.p. 49—50°, α 0, in boiling 0.5N-HCl gives glyceryl α-p-toluenesulphonate, m.p. 54°. The method of Butler *et al.* (A., 1938, II, 341) gives apocupreine β-methoxy-, m.p. 156°, [α] —184° in EtOH (dihydrochloride, [α] —223° in H<sub>2</sub>O), β-ethoxy-, m.p. 111—112°, [α] —179° in EtOH [dihydrochloride, +3H<sub>2</sub>O, [α] (anhyd.) —220° in H<sub>2</sub>O], β-n-propoxy-, m.p. 100—102°, [α] —173° in EtOH (dihydrochloride, [α] —213° in H<sub>2</sub>O), β-n-butoxy-, m.p. 98—99°, [α] —165° in EtOH, and β-α'-phenylethoxyethyl ether (I), m.p. 170—171°, [α] —132° in EtOH (dihydrochloride, [α] —160° in H<sub>2</sub>O), β-γ-isopropylidene-α-glyceryl, m.p. 186—188°, [α] —169° in EtOH, α-glyceryl, amorphous, [α] —167° in EtOH, —266° in 0.1N-HCl [dihydrochloride, +2H<sub>2</sub>O, [α] (anhyd.) —218° in H<sub>2</sub>O], and n-dodecyl ether, m.p. 127°, [α] —145° in EtOH (dihydrochloride, [α] —156° in EtOH, —129° in 0.1N-HCl). The OH·[CH<sub>2</sub>]<sub>2</sub> ether is best prepared by hydrolysis of (I) (cf. *loc. cit.*).

R. S. C.

**Alkaloid of Rauwolfia canescens, Linn. III. Degradation products of rauwolscine.** A. Mookerjee (*J. Indian Chem. Soc.*, 1943, **20**, 11—19).—Rauwolscine (I), which contains 2 active H, gives an Ac derivative, m.p. 216—218° (decomp.), with Ac<sub>2</sub>O and NaOAc. Rauwolscinic acid at 300°/5 mm. yields harman and 3-ethylindole and when fused with KOH gives indole-2-carboxylic acid, isophthalic acid, harman, and an indole. A partial formula for (I) is suggested.

J. H. BA.

**Aconite alkaloids. XV. Kobusine, a new aconite alkaloid.** H. Sugimoto and F. Shimanouti (*Annalen*, 1940, **545**, 220—228).—Kobusine (I), C<sub>20</sub>H<sub>27</sub>O<sub>2</sub>N, m.p. 268°, [α]<sub>D</sub><sup>25</sup> +83.61° in CHCl<sub>3</sub>, is isolated from the residues remaining after removal of jesaconitine from the extracts of *Aconitum sachalinense*, Fr. Schmidt. It gives a hydrobromide (+1H<sub>2</sub>O), m.p. 285° (decomp.), [α]<sub>D</sub><sup>18</sup> +40.68° in H<sub>2</sub>O, hydrochloride (II) (+1.5H<sub>2</sub>O), decomp. 300°, [α]<sub>D</sub><sup>21</sup> +41.4° in H<sub>2</sub>O, anhyd. perchlorate, m.p. 220° (decomp.), platinichloride, red-brown needles or nearly colourless prisms, which blacken at 262°, and picrate, m.p. 277°. (I) cannot be hydrolysed and is stable

towards KOH-EtOH. It does not contain OMe or NHMe but is a *tert.* base since it affords a *methiodide*, m.p. 287° (decomp.). It does not react with CH<sub>3</sub>N<sub>2</sub> or with CO<sub>2</sub> reagents. With AcCl it affords a *diacetate*, m.p. 139—140°. (I) contains 2 double linkings one of which is attached to N since hydrogenation (PtO<sub>2</sub> in AcOH) followed by acetylation (AcCl) affords *triacyltetrahydrokobusine*, m.p. 183—184° (decomp.). (II) is transformed by NaNO<sub>2</sub> into the corresponding *nitrite*, decomp. 242°, softens at 230°. Review of the empirical formulæ of the aconite alkaloids indicates the correctness of those adopted by Majima *et al.* derived from the parent bases C<sub>18</sub>H<sub>28</sub>N and C<sub>20</sub>H<sub>31</sub>N but suggests that atisine is C<sub>22</sub>H<sub>31</sub>O<sub>2</sub>N [instead of C<sub>22</sub>H<sub>33</sub>O<sub>2</sub>N advanced by Lawson *et al.* (A., 1937, II, 527)] and that neoline is C<sub>24</sub>H<sub>39</sub>O<sub>4</sub>N or C<sub>23</sub>H<sub>37</sub>O<sub>5</sub>N and neopelline is C<sub>33</sub>H<sub>45</sub>O<sub>8</sub>N or C<sub>32</sub>H<sub>43</sub>O<sub>8</sub>N (cf. Freudenberg *et al.*, A., 1938, II, 47). H. W.

## VIII.—ORGANO-METALLIC COMPOUNDS.

**Mercurated aryl alkyl ketones.**—See B., 1943, III, 225.

**Mercuri-compounds.**—See B., 1943, II, 247; III, 161, 193.

**Silicon methyl halides.**—See B., 1943, II, 248.

**Tin triphenyl oxide [bis-tin triphenyl ether].** O. Schmitz-Dumont (*Z. anorg. Chem.*, 1941, 248, 289—296).—Dehydration of SnPh<sub>3</sub>·OH with MeCN yields (SnPh<sub>3</sub>)<sub>2</sub>O, m.p. 122—123·5°, which gives SnPh<sub>2</sub>O + SnPh<sub>4</sub> above its m.p., and is easily hydrolysed to SnPh<sub>3</sub>·OH. C. R. H.

**Condensations by sodium. XXVI. Metallation of benzene, toluene, and xylene. Orienting influence of sodium and the influence of alkyl groups on metallation.** A. A. Morton, E. L. Little, jun., and W. O. Strong, jun. **XXVII. Disodium furylene. Aromatic properties of furan.** A. A. Morton and G. H. Patterson (*J. Amer. Chem. Soc.*, 1943, 65, 1339—1346, 1346—1348; cf. A., 1943, II, 114).—XXVI. Dialkylation of C<sub>6</sub>H<sub>6</sub> or PhMe by NaC<sub>5</sub>H<sub>11</sub> in *n*-C<sub>8</sub>H<sub>18</sub> is the main reaction if a small amount of aromatic hydrocarbon is used with vigorous stirring. Thus, after carboxylation, C<sub>6</sub>H<sub>6</sub> gives 51% of *m*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub> (with 4·5% of BzOH), and PhMe gives 40% of *m*-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CO<sub>2</sub>H. Alkylation of xylenes is wholly or mainly nuclear; monometallation and alkylation gives *p*- (36%), *m*- (37%) [*diamide*, m.p. 213—214° (corr.)], and *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub> (19% with a small amount of CO<sub>2</sub>H·C<sub>6</sub>H<sub>3</sub>·CH<sub>2</sub>·CO<sub>2</sub>H). The *m*-orientation for C<sub>6</sub>H<sub>6</sub> and PhMe is explained by the Na derivatives acting as salts, in which the Na is never far distant from the anion; the Na<sup>+</sup> thus exerts a predominating influence on further substitution. Other reactions of organo-metallic compounds are similarly accounted for. The lower reactivity of xylenes, particularly *o*-xylene, is due to the retarding effect of alkyl with, perhaps, accessory steric reasons. XXVII. Furan (method as above) yields furan-2-carboxylic (27%) and -2:5-dicarboxylic acid (6·5%). The *m*-orienting influence of Na is overcome by ether grouping. R. S. C.

## IX.—PROTEINS.

**Experiments with melanin.** E. Kovács and M. Engel (*Magyar Orv. Arch.*, 1941, 42, 225—232).—Melanin reduces ammoniacal solutions of Ag salts to Ag and, owing to its large surface area, fixes the Ag formed. It also retards the reduction of such solutions by aldehydes and the action of blood-catalase on H<sub>2</sub>O<sub>2</sub>. This effect is due to the surface action of the melanin (protective colloid).

M. A. B.  
**Coloured copper complexes formed by the biuret reaction with proteins and protein fission products.** A. Kuntzel and T. Dröscher (*Biochem. Z.*, 1940, 306, 177—204).—NHMeAc and OH·CH<sub>2</sub>·CO·NH·CH<sub>2</sub>·CO<sub>2</sub>Me give no biuret reaction. Deaminated (HNO<sub>2</sub>) glycylglycylglycine ester gives a red colour, whilst NHMe·CO·CH<sub>2</sub>·CO·NHMe gives only a pale blue colour. Structural formulæ advanced by the authors and others for these Cu-peptide complexes are discussed. Whilst peptide complexes are formed only in strongly alkaline solution, NH<sub>2</sub>-acid-Cu complexes are formed in neutral or dil. acid or alkaline solutions. Glycine (I) (2 mols.) forms a complex with Cu (1 mol.) that is stable only in neutral solution; with 4 mols. of (I), 1 mol. of Cu gives in alkaline solution a ppt. of [Cu(NH<sub>2</sub>R·CO<sub>2</sub>Na)<sub>4</sub>](OH)<sub>2</sub>. Optical extinction curves indicate that intact and hydrolysed gelatin form a complex of Cu-(I) type. In dil. acid, neutral, or dil. alkaline solution, proteins give a green or green-blue colour, due to (I)-type reaction with the NH<sub>2</sub> or CO<sub>2</sub>H groups; in conc. alkaline solutions, the red colour due to the stable peptide complex is also present. The formation of basic complexes is also postulated. Colour and extinction data for gelatin (II) at various stages of hydrolysis (NH<sub>2</sub>-N up to 62·8%) and with different ratios of Cu : N indicate that the more complex is the protein product, the greater is the proportion of red component, and that the Cu : N ratio greatly affects the colour. During hydrolysis, not only are NH<sub>2</sub> and CO<sub>2</sub>H groups liberated but also peptide groupings are released from the lattice structure of the intact protein and thus enabled to form their characteristic Cu complexes. With alkaline Cu-protein solutions, the saturation val. of Cu : N ratio, found by Jesserer and Lieben (A., 1937, II, 478) to be 1 : 6, is shown

to be 1 : 2·38 for (II); such systems are probably supersaturated with Cu(OH)<sub>2</sub>. Supersaturation with Cu(OH)<sub>2</sub> does not occur with hydrolysed (II). The normal saturation ratio for caseinogen is 1 : 6·9 and for ovalbumin, 1 : 4·1; the latter gives unstable, supersaturated systems with a ratio as low as 1 : 1·25. (II) alone of the three proteins gives a yellow solution on heating the Cu complex at pH 8·5—9. F. O. H.

**Salmon protein as source of histidine, arginine, lysine, cystine, tyrosine, and tryptophan.** L. Arrigoni and L. Fischer (*J. Amer. Pharm. Assoc.*, 1943, 32, 155—160).—Dried, defatted muscle protein of canned pink salmon (*Oncorhynchus gorbuscha*) contains 1·55, 4·62, 6·22, 1·05, 0·86, and 0·97%, respectively, of the above NH<sub>2</sub>-acids (isolated as such or as derivatives, *e.g.*, picrolonates). F. O. H.

**Dicarboxylic and basic amino-acids of edestin, ovalbumin, and β-lactoglobulin.** A. C. Chibnall, M. W. Rees, and E. F. Williams (*Biochem. J.*, 1943, 37, 372—388).—Following hydrolysis for 23 hr. with 20% HCl, all excess of HCl is removed by repeated evaporation in a vac. after addition of H<sub>2</sub>O. The subsequent fractionation of the hydrolysate requires the adoption of certain definite conditions, in order to minimise the overall loss of N. Cystine and the major part of the aspartic acid must be removed before the introduction of either Ba<sup>++</sup> or SO<sub>4</sub><sup>==</sup>; the excess of either can then be removed as BaSO<sub>4</sub> without appreciable loss of N; Cl<sup>-</sup> can then also be removed as AgCl without loss of N. Where phosphotungstic acid is used to ppt. bases, it can be removed without loss of N by means of C<sub>5</sub>H<sub>11</sub>·OH-Et<sub>2</sub>O, provided that the aq. phase is first saturated with Et<sub>2</sub>O and Et<sub>2</sub>O-H<sub>2</sub>O is used for all aq. washings. Cystine (and residual humin) is removed from hydrolysates, by addition of Cu<sub>2</sub>O, as cysteine Cu<sup>I</sup> mercaptide. Subsequent operations are standard but with observance of the precautions detailed. CuCO<sub>3</sub> must be free from SO<sub>4</sub><sup>==</sup>, Cl<sup>-</sup>, and other metals. 12-Phosphotungstic acid must be N- and Na-free. Ag<sub>2</sub>O and Cu<sub>2</sub>O must be free from salts and alkali, and Ca(OH)<sub>2</sub> free from SO<sub>4</sub><sup>==</sup> and Fe. The overall losses of N in the analysis of edestin, ovalbumin, and β-lactoglobulin are 2·95, 2·86, and 1·25% respectively, of the total protein-N. Vals. for the arginine content of horse carboxyhaemoglobin and cattle haemoglobin throw doubt on the accuracy of Vickery's flavianic acid method in some cases. P. G. M.

**Nitrogen distribution and basic amino-acids in horseradish peroxidase and horse-liver catalase, determined by new micro-method.**—See A., 1943, III, 840.

**Crystalline horse-liver catalase.**—See A., 1943, III, 841.

## X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

**Volatile hydrogenation derivatives of lignin.** A. Bailey (*J. Amer. Chem. Soc.*, 1943, 65, 1165—1168).—Hydrogenation (Raney Ni; 260°/6500 lb.) of Western hemlock lignin in Bu<sup>o</sup>OH and efficient fractionation of the volatile products gives H<sub>2</sub>O 17·9, Pr<sup>β</sup><sub>2</sub> 0·6, MeOH 0·2, tetrahydrofurfuryl alcohol 1·2, EtOH 0·3 (probably derived from CHEt·CMe·CHO), CMe<sub>2</sub>Et·OH 1·0, Bu<sup>o</sup>OH 1·2, and CHMePr<sup>β</sup>·OH 0·3%. Use of Cu chromite gives different products. In H<sub>2</sub>O the products are different from those formed in BuOH or dioxan. The nature of the lignin affects that of the products. R. S. C.

**Properties of lignin esters.** J. J. McNair and E. C. Jahn (*Paper Trade J.*, 1943, 117, TAPPI Sect., 85—89).—Nine esters of lignin (prep. from *Abies grandis*, Lindl., by 70% H<sub>2</sub>SO<sub>4</sub>) and org. acids have solubilities very similar to that of lignin, are completely destroyed by treatment with, alternately, Cl<sub>2</sub> and Na<sub>2</sub>SO<sub>3</sub>, and slowly condense with PhOH, NH<sub>2</sub>Ph, and MeCHO. Some fractionation occurs during esterification with resulting decrease or increase in OMe content, but no loss of OMe. The lignin nitrate is more sol. R. S. C.

**Lignin and related compounds. LXV. Re-ethanolysis of isolated lignins.** W. B. Hewson and H. Hibbert. **LXVI. Ethanolysis of maple wood.** E. West, W. S. MacGregor, T. H. Evans, I. Levi, and H. Hibbert. **LXVII. Isolation and identification of α-4-hydroxy-3:5-dimethoxyphenylpropan-β-one and α-4-hydroxy-3-methoxyphenylpropan-β-one from maple wood ethanolysis products. Metabolic changes in lower and higher plants.** M. Kulka and H. Hibbert. **LXIX. Isolation of α-4-hydroxy-3-methoxyphenylpropan-β-one and α-ethoxy-α-4-hydroxy-3-methoxyphenylpropan-β-one from the ethanolysis products of spruce wood.** E. West, A. S. MacInnes, and H. Hibbert. **LXX. Hydrogenolysis and hydrogenation of maple wood. LXXI. Course of formation of native lignin in spruce buds.** J. R. Bower, jun., L. M. Cooke, and H. Hibbert (*J. Amer. Chem. Soc.*, 1943, 65, 1173—1176, 1176—1180, 1180—1185, 1187—1192, 1192—1195, 1195—1198; cf. A., 1943, II, 301).—LXV. Lignin, obtained from maple wood by repeated treatment for short periods with HCl-EtOH, is treated exhaustively with HCl-EtOH and separated into fractions sol. and insol. in Et<sub>2</sub>O, light petroleum, NaOH, NaHSO<sub>3</sub>, and acid. The monomeric products resemble those obtained by exhaustive ethylation of the wood, proving that

they are derived from the lignin and supporting the view that the process involves polymerisation and depolymerisation.

LXVI. The H<sub>2</sub>O-sol. oils obtained by ethanolysis of maple wood are freed from resin (which causes decomp. of the monomeric fractions) by pouring the solution in COMe<sub>2</sub> into light petroleum and then exhaustively extracted from H<sub>2</sub>O by C<sub>6</sub>H<sub>6</sub> and fractionated as above.

LXVII. The H<sub>2</sub>O-sol. oils (from maple wood) sol. in NaHSO<sub>3</sub> (see above) are converted into oximes, vanillin and syringaldehyde being thus eliminated as non-reactive. Pptn. of the Ni salts then removes diketones. Hydrolysis of the residual oximes by 7N-H<sub>2</sub>SO<sub>4</sub> and fractionation yields 4-hydroxy-3-methoxy- (I), b.p. 115°/0.15 mm. (semicarbazone, m.p. 157—158°; thiosemicarbazone, m.p. 187—188°), and 4-hydroxy-3:5-dimethoxy-benzyl Me ketone (II), m.p. 68—69° (semicarbazone, m.p. 155—156°). Syringaldehyde, EtNO<sub>2</sub>, NH<sub>2</sub>Me.HCl, and Na<sub>2</sub>CO<sub>3</sub> in EtOH at room temp. give β-nitro-α-4-hydroxy-3:5-dimethoxy-Δ<sup>α</sup>-propene, m.p. 103—104°, converted by Fe-FeCl<sub>3</sub>-HCl-H<sub>2</sub>O-EtOH into (II). Vanillin gives similarly β-nitro-α-4-hydroxy-3-methoxyphenyl-Δ<sup>α</sup>-propene, m.p. 101—102°, and thence (I). Hydrogenation in presence of Pd-C in C<sub>6</sub>H<sub>5</sub>N at 65° may replace reduction by Fe-HCl. The products from wood resemble the phenolic acids formed by moulds.

LXIX. Spruce wood yields (I) as above and 3:4:1-OMe·C<sub>6</sub>H<sub>3</sub>(OH)·CH(OEt)·COMe (cf. *loc. cit.*) [as NH<sub>4</sub> salt or semicarbazone; absorption max. at 1060 Å. (*E*<sub>max</sub> 1.66), min. at 1145 Å.; with CrO<sub>3</sub> gives 2 AcOH; yields the known veratrole derivative].

LXX. Hydrogenation of 3:4:1-OH·C<sub>6</sub>H<sub>3</sub>(OMe)·CO·[CH<sub>2</sub>]<sub>2</sub>·OH (III) in presence of Cu chromite in dioxan at 280°/3000 lb. (cold) gives γ-cyclohexylpropan-α-ol (IV) (76%) and 4-n-propylcyclohexanol (V) (24%). The supposedly pure (V) obtained by similar hydrogenation of maple wood or maple ethanol-lignin is shown by improved fractionation to contain much (IV). The results support the view that the terminal chains of lignin are CH<sub>2</sub>·OH or CH<sub>2</sub>·O·C.

LXXI. Hydrogenation (Cu chromite) of mature spruce wood (35—40 years old) gives 1.9% of (V), 1.4% of (IV), and 0.9% of γ-4-hydroxycyclohexylpropan-α-ol. None of these products is obtained from spruce tips 2.5—3 weeks old. Tips which are 3.5—4 months old give 0.8% of (V), i.e., 20% of the lignin products. (III) added prior to hydrogenation increases the yields by the expected amount, thus proving absence of decomp. R. S. C.

Oxidation of solutions of humic acids and related substances. H. Niklas and C. Genninger (*Kolloid-Z.*, 1940, 93, 225—233).—Present knowledge of the effect of oxidising agents on humic acids is discussed with special reference to H<sub>2</sub>O<sub>2</sub> and the catalytic influence of Fe(OH)<sub>3</sub>. C. R. H.

Fumigacin.—See A., 1943, III, 770.

## XI.—ANALYSIS.

Modern methods of preparative organic chemistry. IV. Chromatographic adsorption. H. Brockmann (*Angew. Chem.*, 1940, 53, 384—390).—A review.

Infra-red spectroscopy as an organic analytical tool. R. C. Gore (*J. Chem. Educ.*, 1943, 20, 223—229).—A review. L. S. T.

Simple semi-micro-arrangement for the kinetics of hydrogenation. —See A., 1943, I, 287.

Qualitative test for methoxy- and other alkoxy-groups. W. C. Tobie (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 433—434).—The substance in AcOH is treated with HI in a test-tube which holds a plug of cotton gauze impregnated with Pb(OAc)<sub>2</sub>-NaOH-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, which absorbs interfering substances. Above the plug a test-paper impregnated with Hg(NO<sub>3</sub>)<sub>2</sub>-HNO<sub>3</sub> indicates a positive test by formation of HgI<sub>2</sub> (orange or vermilion). The sensitivity limits are ~5 mg. for vanillin and ~10 mg. for codeine. J. D. R.

Determination of butadiene in presence of other unsaturated and saturated gaseous hydrocarbons. J. F. Cúneo and R. L. Switzer (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 508—509).—The gases are passed through an aq. Hg(NO<sub>3</sub>)<sub>2</sub>-NaNO<sub>3</sub>-HNO<sub>3</sub>, which absorb alkylenes and alkadienes. A sample is also hydrogenated and the mol.-% of alkadiene calc. as the mol.-% unsaturation by hydrogenation minus the mol.-% unsaturation by Hg(NO<sub>3</sub>)<sub>2</sub> absorption. J. D. R.

Macro-molecular compounds. CCXL. Fractionation of multi-molecular substances by partition between two liquid phases. G. V. Schultz and E. Nordt (*J. pr. Chem.*, 1943, [ii], 155, II5—128).—Fractionation of a heterogeneous polymer by partition between two immiscible solvents is considered theoretically. Partition of polyethylene oxide between H<sub>2</sub>O and C<sub>6</sub>H<sub>6</sub>-CHCl<sub>3</sub> (increasing amounts of CHCl<sub>3</sub>) is achieved, the average mol. wt. of material in the org. layer changing progressively from 6500 to 3550. R. S. C.

Sensitivity of chemical reactions. IV. Reactions of organic compounds. Z. Karaoglanov (*Z. anal. Chem.*, 1941, 121, 92—127;

cf. A., 1941, I, 427).—Sensitivities, expressed as μg. per 10 c.c., are tabulated and discussed for certain reactions, carried out under different conditions, of EtOH; CH<sub>2</sub>O; MeCHO; CCl<sub>3</sub>·CHO, H<sub>2</sub>O; furfuraldehyde; COMe<sub>2</sub>; HCO<sub>2</sub>H; lactic acid; tartaric acid, CO(NH<sub>2</sub>)<sub>2</sub>; fructose; glucose; lactose; sucrose; and starch. L. S. T.

Bromatometric determination of l-ascorbic acid (vitamin-C). E. Schulek, J. Kovács, and P. Rózsa (*Z. anal. Chem.*, 1941, 121, 17—20).—The sample containing 1—200 mg. of l-ascorbic acid (I) is dissolved in 10 ml. of H<sub>2</sub>O, 0.5 g. of KBr and 5—10 c.c. of 10% HCl are added, and the solution is titrated with 0.01 or 0.1N-KBrO<sub>3</sub> (p-ethoxychrysoidine hydrochloride). An indicator correction must be applied when 0.01N-KBrO<sub>3</sub> solutions are used. 1 c.c. of 0.1N-KBrO<sub>3</sub> = 8.805 mg. of (I). Typical data are recorded, and the mechanism of the reaction is discussed. L. S. T.

Determination of formaldehyde. R. Wolf (*Rev. Brasil. Quím.*, 1943, 15, 159—162).—Iodometric determination of CH<sub>2</sub>O is preferred. F. R. G.

Identification of organic bases by means of the optical properties of diluturates (nitrobarbiturates). Aliphatic amines. E. M. Plein and B. T. Dewey (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 534—537).—The optical crystallographic data for 22 primary aliphatic amine 5-nitrobarbiturates and for 5-nitrobarbituric acid are described. The optical properties provide a means of identifying pure amines and some mixtures of amines. J. D. R.

Xanthhydrol as reagent for primary amides.—See A., 1943, II, 334.

Sensitivity of chemical reactions. V. Reactions of organic compounds. Z. Karaoglanov (*Z. anal. Chem.*, 1941, 121, 190—209).—Data for well-known reactions of PhOH, NH<sub>2</sub>Ph, resorcinol, pyrogallol, and salicylic acid carried out under varying conditions are tabulated. Certain general conclusions arising from these and data obtained previously (see above) are discussed. Reactions of org. compounds in the reduction of AgNO<sub>3</sub> and Fehling's solution, in the reaction with Br-H<sub>2</sub>O, and the CHI<sub>3</sub> reaction are compared. L. S. T.

Analytical chemistry of the p-hydroxybenzoic esters. F. Reimers (*Z. anal. Chem.*, 1941, 122, 404—418).—Saponification (in aq. solution) and titration to pH 6.8 (using bromothymol-blue and a comparison buffer solution) is possible, but not suitable. Bromination after saponification, using KBrO<sub>3</sub>, excess of KBr and KCl, and keeping for 15 min. in the dark, uses 6 equivs. to give C<sub>6</sub>H<sub>4</sub>Br<sub>3</sub>·OH; the pure esters afford the following vals.: Me 99.7%, Et 99.6%, Pr<sup>a</sup> 99.6%, CH<sub>2</sub>Ph 98.3%. Bromination of the esters uses 4 equivs. to give OH·C<sub>6</sub>H<sub>4</sub>Br<sub>3</sub>·CO<sub>2</sub>R (R = Pr<sup>a</sup>, m.p. 106—109°, R = CH<sub>2</sub>Ph, m.p. 109—110°); the esters in EtOH solution give: Me 99.2%, Et 97.6%, Pr<sup>a</sup> 99.3%, CH<sub>2</sub>Ph 96.5%, and in NaOH solution give: Et 100.9%, CH<sub>2</sub>Ph 97.5%. Combining the two methods gives the degree of hydrolysis of Na salts, which was found to vary in various commercial samples (from 2.6% to 52.0%), and to rise considerably on keeping solutions over periods of 1, 5, 21, and 90 days. Mixtures of esters can be analysed by a micro-refraction method (cf. Kofler, A., 1937, I, 427), by finding the temp. at which *n* is identical with that of a glass powder. The Et ester has *n* 1.5101 at 117.5—118.5°, the Pr<sup>a</sup> ester at 98—99°; the composition of mixtures can be read from a calibration graph (almost linear) to 5%. S. A. M.

Determination of p-benzoquinone and assay of quinhydrone. E. Schulek and P. Rózsa (*Z. anal. Chem.*, 1941, 121, 258—264).—The reduction of benzoquinone (I) to quinol by EtOH in presence of conc. HCl forms the basis of the method. The sample (0.5—50 mg.) is dissolved in 1—4 c.c. of 96% EtOH and then mixed with 5—10 c.c. of 38% HCl. The solution is diluted with H<sub>2</sub>O to make the [HCl] 5 wt.-%, and titrated with 0.005 or 0.05N-Ce(SO<sub>4</sub>)<sub>2</sub> (0.2% p-ethoxychrysoidine) until the red colour changes to yellow. The indicator correction must be determined. 1 c.c. of 0.05N-Ce(SO<sub>4</sub>)<sub>2</sub> = 2.7008 mg. of (I). In assaying quinhydrone, the quinol content is determined directly by titration with Ce(SO<sub>4</sub>)<sub>2</sub>. Typical data obtained by the new method are recorded. L. S. T.

Determination of sodium dehydroisandrosterone sulphate in water or urine.—See A., 1943, III, 780.

Bromatometric determination and quantitative purity testing of cinchona alkaloids containing the vinyl group. E. Schulek and J. Kovács (*Z. anal. Chem.*, 1941, 121, 21—23).—The sample (0.1—0.2 g. of quinine) is dissolved in 10 c.c. of H<sub>2</sub>O, 20 c.c. of 20% HCl and 1 g. of KBr are added, and the solution is titrated with 0.1N-KBrO<sub>3</sub> (p-ethoxychrysoidine hydrochloride), or the solution is over-titrated with 0.1N-KBrO<sub>3</sub>, the excess of which is determined iodometrically. Typical data are given. Tabulated analyses of numerous commercial samples of cinchona alkaloids and their salts show that quinine and its salts, quinidine, cinchonine, and cinchonidine contain considerable quantities of a constituent that cannot be brominated. L. S. T.

DECEMBER, 1943.



## I.—ALIPHATIC.

Conception of the outcome of chemical reactions. Its origin, operation, and limits. M. Trautz (*J. pr. Chem.*, 1943, [ii], 162, 121—147).—A general historical review of the author's views. It is stressed that the activated state involves formation of a new and chemically distinct entity which is an intermediate common to reactants and products. R. S. C.

Proton mobility and influence of substituents, especially carbonyl and sulphonyl. F. Arndt and B. Eistert (*Ber.*, 1941, 74, [B], 423—454).—Theoretical. The following are discussed: characteristics of proton mobility; proton mobility and constitution; simple hydrides and the field effect; increase in acid nature by substituents; mesomerism and resonance; H exchange and the change in acid nature by substituents; kinetics and energy balance of proton mobility; electronic theory of the  $\text{SO}_2$  group. H. B.

Preparation of  $\beta$ -chloro- $\Delta^2$ -butene.—See B., 1943, II, 337.

Macromolecular compounds. CCCXII. Caoutchouc. LV. Halogen derivatives of rubber hydrocarbons. Hermann Staudinger and Hansjürgen Staudinger (*J. pr. Chem.*, 1943, [ii], 162, 148—180; cf. A., 1942, II, 293).— $K_m$  (determined by  $\eta$  at  $20^\circ$ ) for squalene in PhMe and for squalene hexahydrochloride in PhMe,  $\text{CHCl}_3$ , or tetrahydrofuran are  $4.2$  and  $5.4 \times 10^{-4}$  or, after allowance for the differing sp. gr.,  $3.6$  and  $5.9 \times 10^{-4}$  respectively. The reason for the increase due to halogen is obscure. Hydrochlorides of balata (I) and caoutchouc (II) are prepared having mol. wts. (determined osmotically) 45,000—410,000 and  $K_m$  (in PhMe) 0.42—0.79 and  $1.0$ — $1.3 \times 10^{-4}$ , respectively; since (I) and (II) have  $K_m$   $1.2$ — $1.3$  and  $1.7 \times 10^{-4}$ , respectively, the decrease due to halogen is due to ring-shortening by cyclisation of uncertain nature; the cyclisation is also evidenced by low Cl contents, this deficiency being larger for (I) than for (II) in agreement with the respective  $K_m$ . A pronounced fall in  $K_m$  with increasing mol. wt. is shown. Interaction of  $\text{ZnEt}_2$  with the hydrochlorides of (I) and (II) in PhMe- $\text{N}_2$  at  $-20^\circ$ , raised later in steps to  $40^\circ$ , gives ethylpolypranes, from which some HCl has been lost and which have only about half the original degree of polymerisation; products having mol. wt. 50,000—165,000 have  $K_m$  0.72— $0.95 \times 10^{-4}$ , changes from the hydrochlorides being relatively slight. If the decrease in  $K_m$  for the hydrochlorides had been due to crumpling of a long chain under the influence of the Cl, replacement of the Cl by Et should have returned  $K_m$  to approx. its original val. Absence of such a return confirms the view that the hydrochlorides are cyclised products. The product formed from (I) and HBr at  $0^\circ$  is very unstable; a "dibromide" (56.16% Br; theory 70%) had  $K_m$   $0.61 \times 10^{-4}$ , indicating cyclisation also in this case. Chloroprene, having mol. wt. 115,000, has  $K_m$   $1.65 \times 10^{-4}$ , thus resembling (I), (II), and Buna, and further confirming the cyclisation of the hydrochlorides. Laboratory preps. of chloro-caoutchouc, 'balata, and -Buna 85, and three technical chloro-rubbers, having 54.90—65.92% of Cl and mol. wt. 82,000—410,000, have  $K_m$  0.30— $0.49 \times 10^{-4}$  in PhMe; the very low  $K_m$ , similar to that of cyclocaoutchouc, indicates much cyclisation, in which the side-chains probably participate; this is confirmed by inactivity of the Cl-products towards LiMe, LiPh, and  $\text{ZnEt}_2$  (cf. the pinene hydrochloride derivative,  $\text{C}_{10}\text{H}_8\text{Cl}_{10}$ ); this polycyclic polyterpene structure explains also the stability of the chloro-rubbers and thus their suitability for use in varnishes.  $K_m$  for various rubber derivatives are compared and low vals. explained as due to cyclisation in all cases.  $\eta$  increases with concn., particularly for the long mols. (high  $K_m$ ). When rubber and its derivatives are stretched, the small aggregates of long mols. are compressed laterally into large aggregates, which then act as crystals under X-rays; plasticisers function by easing the sliding of these aggregates over one another. The elasticity is due to deformation of the side-chains during stretching (compression); its extent thus depends on the nature of the branching and side-chains. Purification of the products examined is described. R. S. C.

Configuration of  $\Delta^2$ -butadiene.—See A., 1943, I, 295.

Absorption of light by organic molecules and ions according to quantum mechanics.—See A., 1943, I, 295.

Assignment of absorption bands in conjugated systems of chromophores.—See A., 1943, I, 296.

Effect of acidifying substituents on chromophoric systems.—See A., 1943, I, 296.

Physico-chemical properties of chromophoric groups.—See A., 1943, I, 296.

Conjugation of chromophores and constitution of organic compounds.—See A., 1943, I, 296.

Production of carbon tetrachloride.—See B., 1943, II, 306.

Influence of oxygen and sulphur atoms on the velocity of hydrolysis of the carbon-halogen bond.—See A., 1943, I, 310.

Catalytic action of activated silica-alumina. Action of activated clay on *n*-octyl alcohol and cyclohexanone. A. V. Frost (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 37, 223—225).—Boiling *n*- $\text{C}_8\text{H}_{17}\text{OH}$  and activated Caucasian clay with removal of  $\text{H}_2\text{O}$  gives  $\text{C}_8\text{H}_{16}$  33%,  $\text{C}_8\text{H}_{14}$  4%,  $\text{C}_{16}\text{H}_{34}$  6%,  $\text{C}_{16}\text{H}_{32}$  4%, higher saturated (2%) and unsaturated hydrocarbons 13%, tar 2%,  $\text{H}_2\text{O}$  11%, gas and losses 17%, and other products 5%. Boiling cyclohexanone with the clay gives  $\text{C}_6\text{H}_6$  (~5%), cyclohexane, methylcyclopentane, and PhOH. R. S. C.

Marine products. XIV. Astrol.—See A., 1943, III, 895.

Diphenylurethane of nerol. Y. R. Naves and A. V. Grampoloff (*Helv. Chim. Acta*, 1943, 26, 1393).—Contrary to the suggestion of Palfray *et al.* (*Bull. Soc. chim.*, 1943, [v], 10, 131), the diphenylurethane of nerol, m.p.  $52^\circ$ , is a well-defined individual. H. W.

Benzoylation of erythritol and preparation of derivatives of *O*-benzoylglycollaldehyde. H. Ohle and G. A. Melkonian (*Ber.*, 1941, 74, [B], 291—294; cf. A., 1943, II, 393).—*meso*-Erythritol (I) and 5 mols. of  $\text{BzCl}$  in  $\text{C}_5\text{H}_5\text{N}$  afford 98% of *meso*-erythritol tetrabenzoate (II), m.p. 188—188.5°. (I) and 2 mols. of  $\text{BzCl}$  afford some (II), with the 1:4-*di*- (III), m.p. 148°, and 1:2:4(?) *tri*-benzoate, m.p. 108—108.5°. (III) and  $\text{Pb}(\text{OAc})_4$  in  $\text{C}_6\text{H}_6$  afford  $\text{OBz}\cdot\text{CH}_2\cdot\text{CHO}$  [phenylhydrazone (unstable), m.p. 80—81°; 2:4-dinitrophenylhydrazone, m.p. 185°] and an isomeric erythritol 1:3(?) *dibenzoate*, m.p. 142°, already present in the (III) used. J. W.

Synthesis of optically active  $\beta$ -phosphatidic acids. E. Baker, I. B. Cushing, and H. O. L. Fischer (*Canad. J. Res.*, 1943, 21, B, 119—124).—*dl*- and *l*(-)-Glycerol  $\alpha$ -benzoate, m.p. 66.5—67°,  $[\alpha]_D -16.8^\circ$  in EtOH [from *d*(+)-isopropylideneglycerol benzoate and aq. AcOH at  $80^\circ$ ], with  $\text{CPh}_3\text{Cl}$  in quinoline at  $100^\circ$ , then at room temp., yield respectively *dl*-, m.p. 124—125°, and *l*- $\gamma$ -triphenylmethylglycerol  $\alpha$ -benzoate, m.p. 89—90°,  $[\alpha]_D -12.6^\circ$  in EtOH,  $-22.1^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ ,  $-11.5^\circ$  in  $\text{C}_6\text{H}_6$ , which with  $\text{POCl}_3$  in  $\text{C}_5\text{H}_5\text{N}$ , then  $\text{K}_2\text{CO}_3$  under  $\text{Et}_2\text{O}$ , yield *K dl*-, m.p. 174—175° (bath preheated to  $145^\circ$ , then heated at  $10^\circ$  per min.), and *l*- $\alpha$ -benzoyl- $\gamma$ -triphenylmethyl- $\beta$ -glycerophosphate, m.p. 174—175°, converted by reduction ( $\text{H}_2$ , Pd) or hydrolysis (dil. HCl at room temp.) into *K dl*- and (impure) *l*- $\alpha$ -benzoyl- $\beta$ -glycerophosphate,  $[\alpha]_D +9^\circ$  in  $\text{H}_2\text{O}$ , respectively. A. Li.

Production of sodium formate.—See B., 1943, II, 307.

Thermal decomposition of *n*- and *iso*-propyl formates.—See A., 1943, I, 309.

Catalytic oxidation of hydroxylated and unsaturated fatty acids.—See B., 1943, II, 339.

Inhibitors of the enzymic oxidation of unsaturated fatty acids.—See A., 1943, III, 915.

Investigation of the metabolism of fats with deuterium as indicator. II. Formation of oleic acid from carbohydrates.—See A., 1943, III, 904.

Esters of glycollic acid.—See B., 1943, II, 307.

Preparation of lactic acid.—See B., 1943, II, 338.

Effect of citrate on rotation of molybdate complexes of malate, citramalate, and isocitrate. H. A. Krebs and L. V. Eggleston (*Biochem. J.*, 1943, 37, 334—338; cf. Auerbach and Krüger, A., 1923, ii, 884; B., 1924, 32).—The optical rotation of the molybdate complexes of malic, citramalic, and isocitric acid is increased by citrate, the magnitude of the increase (sometimes >100%) depending on the concn. of the substances. Account must be taken of this in the polarimetric determination of the acids by the molybdate



ation of freshly distilled aldol is complete in ~4 hr.; there is no alteration in mol. wt. of each sample over a period of several hr. In one case, when an aq. solution of viscous aldol was kept for several weeks, there was a gradual fall in mol. wt. In AcOH (favors polymerisation), the mol. wt. is independent of the age of the aldol and corresponds to 20% of monomeric + 80% of dimeric. Freshly distilled aldol and a small amount of AcOH or BzOH show a rise in temp. and a marked increase in  $\eta$  in ~10 min.; with quinol, pyrogallol,  $\alpha$ - or  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH, or *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH, the sample becomes viscous in ~1 hr., thus behaving like pure aldol. A. T. P.

**Dimeric glyceraldehyde  $\alpha$ -diphosphate.** E. Baer and H. O. L. Fischer (*J. Biol. Chem.*, 1943, 150, 213—221).—Successive addition of PPh<sub>2</sub>OCl and  $\gamma$ -glyceraldehyde to dry C<sub>5</sub>H<sub>5</sub>N at 10—15° and subsequently at room temp. gives *glyceraldehyde  $\alpha$ -di(diphenyl phosphate)*, m.p. 110—111°, transformed by catalytic hydrogenolysis in MeOH with H<sub>2</sub> and PtO<sub>2</sub> at room temp. into dimeric glyceraldehyde  $\alpha$ -diphosphate (I), CH<sub>2</sub>R·CH< $\begin{smallmatrix} \text{O} \cdot \text{CHR} \\ \text{CHR} \cdot \text{O} \end{smallmatrix}$ >CH·CH<sub>2</sub>R [R = O·PO(OH)<sub>2</sub>], identified as the Ba<sub>2</sub>H<sub>4</sub> (+2H<sub>2</sub>O) and Ca<sub>2</sub>H<sub>4</sub> (+2H<sub>2</sub>O) salts. The normal Ca and Ba salts are amorphous. Short acid hydrolysis of (I) gives glyceraldehyde  $\gamma$ -phosphate whereas prolonged hydrolysis leads to AcCHO. Towards alkali (I) is remarkably stable. A hydrolysis by phosphatases from dog faeces at pH 9.6 is described.

[By O. Meyerhof.] (I) has been tested for biological activity directly, after partial acid hydrolysis and after incubation with alkali. The negative results show that a substance of constitution and configuration such as (II) cannot be the expected intermediary between glyceraldehyde  $\gamma$ -phosphate and glyceric acid  $\alpha$ -diphosphate in carbohydrate metabolism. H. W.

**Synthesis of *dl*-glyceraldehyde  $\gamma$ -phosphate.** E. Baer and H. O. L. Fischer (*J. Biol. Chem.*, 1943, 150, 223—229).—Dimeric glyceraldehyde  $\alpha$ -di(diphenyl phosphate) is converted by 30—32% HBr in AcOH at room temp. into *glyceraldehyde  $\alpha$ -bromide  $\gamma$ -Ph<sub>2</sub> phosphate* (dimeric) (I), CH<sub>2</sub>R·CH< $\begin{smallmatrix} \text{CHBr} \cdot \text{O} \\ \text{O} \cdot \text{CHBr} \end{smallmatrix}$ >CH·CH<sub>2</sub>R [R = O·PO(OPh)<sub>2</sub>], m.p. 161—162°, and by HCl in pure dioxan into the corresponding dimeric  *$\alpha$ -chloride* (II), m.p. 146—147°. (II) with 2:4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·NH·NH<sub>2</sub> in boiling 2.5N-HCl affords methylglyoxal-2:4-dinitrophenylosazone (III) in 97% yield. (I) is converted by reductive cleavage with PtO<sub>2</sub> and H<sub>2</sub> in dry AcOH or, preferably, by treatment with boiling 4% AcOH-COMe<sub>2</sub> into *glyceraldehyde  $\alpha$ -bromide  $\gamma$ -H<sub>2</sub> phosphate (dimeric)* (IV), best purified as its additive product (V) with 2 mols. of dioxan. N-HCl at 100° for 1 hr. or N-NaOH for 20 min. at room temp. liberates 99.4 and 96.0% respectively of the H<sub>3</sub>PO<sub>4</sub> from (V), which also gives (III) when treated with 2:4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·NH·NH<sub>2</sub>. (IV) and (V) are readily hydrolysed to glyceraldehyde  $\gamma$ -H<sub>2</sub> phosphate, best isolated as the Ca salt. H. W.

**General methods for the formation of ketens.** C. F. Hurd, F. W. Cashion, and P. Perletz (*J. Org. Chem.*, 1943, 8, 367—372).—No general method of preparing CHR:C:CO exists. Zn and CH<sub>2</sub>Br·COBr (I) give HBr, EtOAc, CH<sub>2</sub>Br·CO<sub>2</sub>Et, and CH<sub>2</sub>Br·CO·CHBr·COBr (characterised by conversion by aq. NH<sub>3</sub> and then aq. Br into  *$\alpha$ -tribromoacetoacetamide*, m.p. 118°). Keten is also not obtained from (I) by Cu-bronze (gives HBr), Na (gives HBr), Mg (no reaction), or Mg + MgI<sub>2</sub>·Et<sub>2</sub>O·N<sub>2</sub> (gives I). CH<sub>2</sub>Cl·CO<sub>2</sub>Et with Zn gives HCl and with Mg + MgI<sub>2</sub> or NaI gives I, but no keten. OAc·CHMe·COBr, b.p. 160°, and Zn in Et<sub>2</sub>O give HBr but no CHMe:C:CO. R. S. C.

**Oxidation of ketones.**—See B., 1943, II, 339.

**Bromination of ketones.**—See B., 1943, II, 308.

**Autoxidation of  $\Delta^2$ -unsaturated ketones. I. Peroxide formation and association processes.** H. Albers and W. Schmidt (*J. pr. Chem.*, 1943, [ii], 162, 91—112).—Thin films of CHMe:CH·COMe (I) evaporate, leaving a very small, soft residue. Those of CHMe:CH·CH:CH·COMe (II) rapidly change to a resin. Passing O<sub>2</sub> through (I) at 20±0.05° leads to absorption of ~0.5 atom of O and formation of <1% of peroxide but of much MeCHO. Similar passage of O<sub>2</sub> through (II) gives a peroxide very rapidly, with only traces of CO<sub>2</sub> and MeCHO; up to 1.75—1.8 atoms of O are absorbed before the liquid becomes too viscous to allow passage of gas. The peroxidic product (III) explodes when heated. Quant. measurements during the reaction indicate dimerisation of the peroxide, which is confirmed by determination of mol. wts.  $\eta_{sp}$  increases enormously during the reaction (from 1.46 to 14.614), this being ascribed to association rather than to polymerisation by primary valencies; the *trans*-form of the dimeric peroxide,

CHAc:CH·CH< $\begin{smallmatrix} \text{O} \cdot \text{O} \cdot \text{CHMe} \\ \text{CHMe} \cdot \text{O} \cdot \text{O} \end{smallmatrix}$ >CH·CH:CHAc, is particularly suited to give linear aggregates leading to high  $\eta$ . The resins of the films are formed by decomp. of the peroxide, probably with concomitant polymerisation by primary valencies. (III) is readily sol.; it is thixotropic in C<sub>6</sub>H<sub>6</sub>; thermal dissociation occurs at higher temp. (e.g., 50°). Inability to polymerise accounts for inability of (III) to catalyse polymerisation of styrene. R. S. C.

**Alkylation of hydrazine.** O. Westphal (*Ber.*, 1941, 74, [B], 759—776).—Alkylation of N<sub>2</sub>H<sub>4</sub> with AlkHal generally proceeds thus: N<sub>2</sub>H<sub>4</sub> → NH<sub>2</sub>·NHAlk → NH<sub>2</sub>·NAlk<sub>2</sub> → NH<sub>2</sub>·NAlk<sub>3</sub>Hal (I). If, however, Alk has a large vol. (e.g., Pr<sup>8</sup>, CH<sub>2</sub>Ph) formation of (I) is hindered or prevented, and NHAlk·NAlk<sub>2</sub> (II) or, under favourable conditions, (NAlk<sub>2</sub>)<sub>2</sub> results. Formation of (II) is also favoured by use of AlkCl, the reactivity of which decreases with increase in chain-length. If the reaction is carried out at >110° with AlkCl the yield of (I) falls and that of (II) rises (max. at 150—160° and diminishes at >170°). Formation of (I) is favoured when Alk is small but none results when AlkCl is >C<sub>8</sub>H<sub>17</sub>Cl, at which point the yield of (II) also begins to fall and is nil at >C<sub>12</sub>H<sub>25</sub>. MeCl could not be used since the reactions are usually carried out in glass tubes. Reaction proceeds differently when, e.g., a steel autoclave is used; the lower AlkCl thus give unsaturated hydrocarbons, NH<sub>3</sub>, NH<sub>4</sub>Cl, and evil-smelling bases. The following (II) are obtained, usually with mono- and di-substituted hydrazines, from N<sub>2</sub>H<sub>4</sub> (~1.25 mols.), AlkCl (~1 mol.), and sufficient EtOH to give a homogeneous solution at 150—155° unless stated otherwise: *triethyl-* (9.5%), b.p. 43—44°/30 mm., *triallyl-* (12% at 100°), b.p. 61—63°/11 mm., *tripropyl-* (25%), b.p. 59—61°/11 mm. [with (CH<sub>3</sub>CO)<sub>2</sub>O in boiling C<sub>6</sub>H<sub>6</sub> gives *maleic monotripropylhydrazide*, m.p. 65—66°], *tributyl-* (36%), b.p. 102—104°/11 mm. (15% of NH<sub>2</sub>·NBu<sub>3</sub>Cl also formed; *maleic monotributylhydrazide*, m.p. 60—61°), *triheptyl-* (42%), b.p. 172—174°/14 mm. (*maleic monotriheptylhydrazide*, m.p. 57—58°), and *trioctyl-hydrazine* (34%), b.p. 186—187°/4 mm. These are colourless, stable liquids which are somewhat sensitive to O<sub>2</sub> at high temp., reduce aq. NH<sub>3</sub>·AgNO<sub>3</sub> in the cold, are not affected by yellow HgO, are weak to very weak bases, and show 1 active H (Zerevitinov at 90°; ~0.33 at 25°); the viscosity rises with increased C content. Pr<sup>8</sup>Cl at 150° gives NN- or NN'-diisopropylhydrazine (49%), b.p. 32—34°/12 mm.; *sec*-BuCl at 145° affords a *disec*-butylhydrazine (28%), b.p. 86—87°/11 mm.; Bu<sup>7</sup>Cl in boiling MeOH gives *tert*-butylhydrazine hydrochloride, m.p. 202° (after sublimation; transformation point at 122°). The following are also described: *mono*-, b.p. 80—81°/14 mm., and *di*-hexyl-, b.p. 138—140°/14 mm., *mono*-, b.p. 112—114°/12 mm., and *di*-octyl-, b.p. 185—187°/12 mm., m.p. ~26° (*Ac* derivative, m.p. 81—82°), *mono*-, b.p. 176—177°/15 mm., m.p. 31° (*hydrochloride*, m.p. 68°), and *di*-dodecyl-, m.p. 55.5° [oxidised (HgO in C<sub>6</sub>H<sub>6</sub>) to *tetradodecyltetrazen*, m.p. 52.5°], *mono*-, m.p. 57—58° (*hydrochloride*, m.p. 84°), and *di*-hexadecyl-hydrazine, m.p. 74—75° (corresponding tetrazen, m.p. 70°). NHMe·NH<sub>2</sub> and C<sub>12</sub>H<sub>25</sub>Cl in EtOH at 110° give *N*-methyl-*N*-dodecylhydrazine (82%), b.p. 150—153°/11 mm., m.p. ~18° (corresponding tetrazen, m.p. 39°; methiodide, m.p. 126°; ethobromide, m.p. 82°). Cyclic *maleic monododecylhydrazide* is described. Prep. of (NAlk<sub>2</sub>)<sub>2</sub> from (II) is best carried out with AlkBr (1.5—2 mols.) and an equiv. amount of freshly pptd., finely divided Mg(OH)<sub>2</sub> in EtOH at 140—150°. In the absence of alkali decomp. occurs; KOH is unsatisfactory since it causes olefine formation. (NAlk<sub>2</sub>)<sub>2</sub> are unstable to acids at high temp.; when not quite pure they alter slowly in light. *Tetra-propyl*-, b.p. 88.6—89.9°/11 mm., and *-butyl-hydrazine*, b.p. 133—134°/12 mm., are described. H. B.

**Synthesis of  $\delta$ -diethylaminoisoamylamine required for the manufacture of atebrian.** P. C. Guha, P. L. N. Rao and T. G. Verghese (*Current Sci.*, 1943, 12, 82—83).—NEt<sub>2</sub>·CH<sub>2</sub>·CHO·HCl and COMe<sub>2</sub> yield  *$\alpha$ -diethylamino- $\Delta^2$ -penten- $\delta$ -one*, b.p. 103—105°/30 mm., reduced (Raney Ni) to NEt<sub>2</sub>·[CH<sub>2</sub>]<sub>3</sub>·COMe. CH<sub>2</sub>Cl·CH(OEt)<sub>2</sub> with COMe<sub>2</sub> gives  *$\alpha$ -chloropentan- $\beta$ -ol- $\delta$ -one*, b.p. 128°/15 mm., which could not be dehydrated. F. R. G.

**Reaction between chlorohydrins and ammonia or amines. I. Reaction mechanism.** L. Smith [with T. Nilsson] (*J. pr. Chem.*, 1943, [ii], 162, 63—70).—For interaction of  *$\alpha$ -chlorohydrin* with an excess of dil. aq. NH<sub>3</sub>, NaOH, and CHPhMe·NH<sub>2</sub> (I) at 20°,  $k = 5.63 \pm 0.08$  to  $5.84 \pm 0.12$  (58.0 at 40°),  $6.07$  (62.0 at 40°), and  $5.3$ — $5.9$ , respectively, proving that the rate-controlling step in the reaction with the amines is formation of glycidic (II). For interaction of (II) with an excess of *d*-(I) or 0.0554N-NH<sub>3</sub> at 20°,  $k = 0.0133$  and (up to 40% reaction)  $0.0038$ — $0.00365$ , respectively. For analysis of the reaction mixture containing NH<sub>3</sub>, 99% of the remaining NH<sub>3</sub> is removed in 10 min. by distillation at ~14 mm. For interaction of epichlorohydrin with NH<sub>3</sub> or (I) at 20°,  $k = 0.0175$  and  $0.050$ — $0.051$ , respectively. R. S. C.

**Monoalkylation of ethylenediamine with alkylene oxides.** L. J. Kitchen and C. B. Pollard (*J. Org. Chem.*, 1943, 8, 342—343).—By use of an excess of diamine, (CH<sub>2</sub>)<sub>2</sub>O,  *$\alpha$* , *$\beta$* -epoxy-*n*-propane or -isobutane, or styrene oxide gives good yields of mono(hydroxyalkyl) compounds. Thus are obtained (in MeOH at 40—50°) *N*- $\beta$ -hydroxy-*n*-propyl- (41%), b.p. 112°/10 mm. (*dihydrochloride*, m.p. 184.7—185°; picrate, m.p. 191—192.5°; phenylthiocarbamide derivative, m.p. 149.8—150°), *N*- $\beta$ -hydroxy- $\beta$ -methylpropyl- (87%), b.p. 103.7°/10 mm. [*dihydrochloride*, m.p. 195.7—196.4°; picrate, m.p. 198.5—200.5° (decomp.)], *N*- $\beta$ -hydroxy- $\beta$ -phenylethyl-, m.p. 76—80°, b.p. 184.8°/10 mm. (*dihydrochloride*, m.p. 196.7—200.8°), and *N*- $\beta$ -hydroxyethyl-ethylenediamine, b.p. 123°/10 mm. [picrate, m.p. 224° (decomp.)]; *dihydrochloride*, m.p. 114.3—115.2°. M.p. are corr. R. S. C.

**Preparation of amino-ethers and their acyl derivatives.**—See B., 1943, II, 339.

**Determination of amino-acids.**—See A., 1943, II, 404.

**Amino-acid esters.**—See B., 1943, II, 339.

**Preparation of  $\beta$ -alanine.** F. Weygand (*Ber.*, 1941, 74, [B], 256—257).— $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  is hydrogenated at 40 atm. in  $\text{AcOH}$  containing  $\text{PtO}_2$  and conc.  $\text{H}_2\text{SO}_4$  to 74% of  $\beta$ -alanine Et ester, b.p. 55—56°/9—10 mm., hydrolysed  $[\text{Ba}(\text{OH})_2]$  to 72% of  $\beta$ -alanine, m.p. 195°.

J. WA.

**Amino-acid composition of tyrosidine.** *NN'*-Diacetyl-*l*-ornithine, m.p. 156°,  $[\alpha]_D^{25} + 6.3^\circ$  in  $\text{EtOH}$ .—See A., 1943, III, 846.

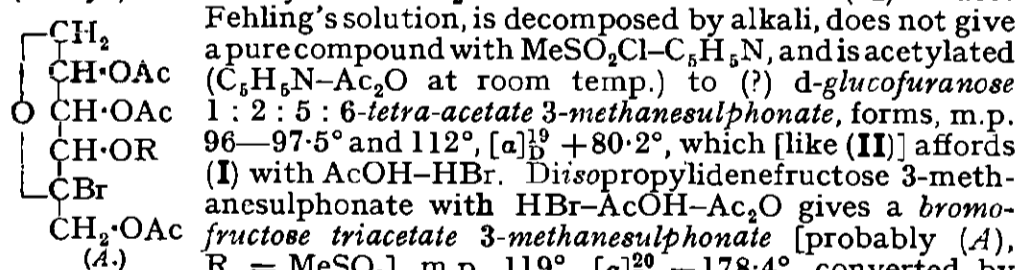
**Preparation of cystine, methionine, and homocystine containing radioactive sulphur.** A. M. Seligman, A. M. Rutenburg, and H. Banks (*J. clin. Invest.*, 1943, 22, 275—279).—Radioactive  $\text{CH}_2\text{Ph}\cdot\text{SH}$  (prep. using S or  $\text{H}_2\text{S}$  from active  $\text{BaSO}_4$ ) was converted into radioactive S-benzylhomocystine by way of  $\text{CH}_2\text{Ph}\cdot\text{S}\cdot[\text{CH}_2]_2\cdot\text{Cl}$  and the phthalimidomalonate, and this was converted into methionine (21% yield) by Na-BuOH (giving radioactive *dl*-homocystine; yield 24%) followed by MeI. The synthesis of radioactive *dl*-cystine (21.5% yield) from  $\text{CH}_2\text{Ph}\cdot\text{SH}$  via  $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CH}_2\text{Cl}$  and S-benzylcystine is also described. In each case 0.06 mol. of radioactive  $\text{BaSO}_4$  was used.

**Resolution of *dl*-pantothenic acid with cinchonidine.** R. Kuhn and T. Wieland (*Ber.*, 1941, 74, [B], 218).—The biologically inactive (–)-form of pantothenic acid (I) forms the less sol. salt with quinine, which is therefore not particularly suitable for isolating the biologically active (+)-(I). Cinchonidine, however, affords *cinchonidine* (+)-*pantothenate* (II), m.p. 178—179°,  $[\alpha]_D^{19} - 62.8^\circ$  in  $\text{H}_2\text{O}$ , as the less sol. salt. The biological activity of (II), calc. in terms of (+)-(I), is twice that of the racemate.

J. WA.

## II.—SUGARS AND GLUCOSIDES.

**Esters of methanesulphonic acid in the sugar group.** IV. B. Helferich and H. Jochinke (*Ber.*, 1941, 74, [B], 719—725).—Contrary to previous work (A., 1939, II, 468), 1 : 2-isopropylidene-glucosulphate 5 : 6-diacetate 3-methanesulphonate is converted by  $\text{HBr}\cdot\text{AcOH}\cdot\text{Ac}_2\text{O}$  into 1 : 2-*a*-bromoethylidene-glucosulphate 5 : 6-diacetate 3-methanesulphonate (I), which with  $\text{C}_6\text{H}_5\cdot\text{MeOH}\cdot\text{C}_6\text{H}_5\text{N}$  at room temp. gives the 1 : 2-*a*-methoxyethylidene derivative, m.p. 160—161° (sinters ~156°),  $[\alpha]_D^{20} + 13.1^\circ$  (corresponding  $\alpha$ -amyloxy-, m.p. 91.5°,  $[\alpha]_D^{21} + 5.1^\circ$ , and  $\alpha$ -benzyloxy-compound, m.p. 132°,  $[\alpha]_D^{21} + 0.49^\circ$ ) (undergoes quant. elimination of the 5- and 6-Ac with aq.  $\text{MeOH}\cdot\text{NaOH}$  at 30°).  $\text{Ag}_2\text{CO}_3$  and (I) in moist  $\text{COMe}_2$  give, with difficulty, *d*-glucosulphate 2(?) : 5 : 6-triacetate 3-methanesulphonate (II), m.p. 119°,  $[\alpha]_D^{19}$  (in  $\text{EtOH}$ )  $+ 22.4^\circ$  (20 min.)  $\rightarrow + 17.4^\circ$  (3 days) when recryst. from  $\text{H}_2\text{O}$ ,  $[\alpha]_D^{20}$  (in  $\text{EtOH}$ )  $+ 59.6^\circ$  (15 min.)  $\rightarrow + 17.2^\circ$  (7 days) when recryst. from  $\text{H}_2\text{O}$  and then from  $\text{EtOH}$ . (II) reduces



H. B.

**Thiocyanic esters of glucose and cellobiose.** A. Müller and A. Wilhelms (*Ber.*, 1941, 74, [B], 698—705).—6-*p*-Toluenesulphonates (but not the *sec.* esters) of sugar derivatives are converted by KCNS in abs.  $\text{COMe}_2$  at 130° (sealed tube) into 6-thiocyanates. Thus  $\beta$ -glucose tetra-acetate 6-*p*-toluenesulphonate gives 47% of  $\beta$ -glucose tetra-acetate 6-thiocyanate, m.p. 117—118°,  $[\alpha]_D^{21} + 27.9^\circ$ , converted by  $\text{AcOH}\cdot\text{HBr}$  at room temp. into 1-bromo- $\alpha$ -glucose triacetate 6-thiocyanate, m.p. 160°,  $[\alpha]_D^{20} + 212.1^\circ$ , which with  $\text{Ag}_2\text{CO}_3$  in  $\text{MeOH}$  affords  $\beta$ -methylglucoside triacetate 6-thiocyanate, m.p. 135°,  $[\alpha]_D^{21} + 15.6^\circ$ , also obtained from the corresponding 6-*p*-toluenesulphonate.  $\alpha$ -Methylglucoside triacetate 6-thiocyanate, m.p. 101—103°,  $[\alpha]_D^{21} + 154.8^\circ$  (from the 6-*p*-toluenesulphonate), with  $\text{n-MeOH}\cdot\text{NaOMe}$  at room temp. and reacylation gives *di*- $\alpha$ -methylglucosidyl 6 : 6'-disulphide hexa-acetate, m.p. 157°,  $[\alpha]_D^{21} + 254^\circ$ . Contrary to Fischer (A., 1914, i, 662), acetobromoglucose and KCNS in  $\text{COMe}_2$  give 1-thiocyanoglucose tetra-acetate (I), m.p. 132—133°,  $[\alpha]_D^{19} - 20.9^\circ$  (+  $\frac{1}{2}$   $\text{COMe}_2$ ),  $-21.8^\circ$  ("anhyd."), converted by  $\text{n-MeOH}\cdot\text{NaOMe}$  and reacylation into isothiotrehalose octa-acetate (poor yield),  $[\alpha]_D^{19} - 45.4^\circ$ , and by  $\text{MeOH}\cdot\text{NH}_3$  into diglucosylamine octa-acetate. (I) reduces Fehling's solution with pptn. of  $\text{CuS}$ . At 141°/14 mm. or in boiling xylene, (I) rearranges to glucose tetra-acetate 1-thiocarbimide (*loc. cit.*),  $[\alpha]_D^{20} + 1.9^\circ$ , which with  $\text{MeOH}\cdot\text{NH}_3$  and  $\text{AlkOH}$  gives 1-glucosylthiocarbimide, m.p. 210—212° (decomp.) (lit. 215—216°), and the corresponding *Me*, m.p. 182—184°,  $[\alpha]_D^{20} + 13.6^\circ$ ,

and Et thiocarbamate,  $[\alpha]_D^{21} + 18.4^\circ$ , respectively. Acetobromocellobiose and  $\text{COMe}_2\cdot\text{KCNS}$  afford only cellobiose hepta-acetate 1-thiocarbimide (+  $2\text{COMe}_2$ ), m.p. 205—206°,  $[\alpha]_D^{20} - 8.6^\circ$ , m.p. ("anhyd.") 208—209°, whence the *Me*, m.p. 207—209°,  $[\alpha]_D^{20} + 12.8^\circ$ , and Et thiocarbamate, m.p. 198°,  $[\alpha]_D^{21} + 30.7^\circ$ .  $[\alpha]$  are in  $\text{CHCl}_3$ .

H. B.

**2 : 6-Dimethylglucose.** K. Freudenberg and G. Hüll (*Ber.*, 1941, 74, [B], 237—244; cf. A., 1943, II, 256).—2 : 6-Dimethylglucose (I) forms two highly cryst. tris(azobenzoyl) derivatives and hence the presence of (I) in the hydrolysis product from fully methylated potato starch cannot be overlooked, nor can (I) arise from hydrolysis of 2 : 3 : 6-trimethylglucose. Glucose,  $\text{H}_3\text{BO}_3$ ,  $\text{COMe}_2$ , and conc.  $\text{H}_2\text{SO}_4$  afford 1 : 2-isopropylidene-*d*-glucosulphate 3 : 5-monoborate (II), m.p. 90—100°, which is acetylated ( $\text{Ac}_2\text{O}$ ,  $\text{NaOAc}$ ) and hydrolysed to 1 : 2-isopropylidene-*d*-glucosulphate 6-acetate (III);  $\text{Ac}_2\text{O}$  and  $\text{C}_6\text{H}_5\text{N}$  afford (III) and much 1 : 2-isopropylidene-glucose 3 : 5 : 6-triacetate. (II),  $\text{C}_6\text{H}_5\text{N}$ , and  $(\text{OMe}\cdot\text{CH}_2\cdot\text{CO})_2\text{O}$  afford 1 : 2-isopropylidene-*d*-glucosulphate 6-methoxyacetate, m.p. 95°. (III),  $\text{PhCHO}$ , and  $\text{ZnCl}_2$  (better than  $\text{P}_2\text{O}_5$ ) give 3 : 5-benzylidene-1 : 2-isopropylidene-glucose 6-acetate, which, with  $\text{KOH}\cdot\text{Me}_2\text{SO}_4$ , gives 3 : 5-benzylidene-6-methyl-1 : 2-isopropylidene-glucosulphate (IV) and some 3 : 5-benzylidene-1 : 2-isopropylidene-glucosulphate, m.p. 148.5—150°. (IV) gives on hydrolysis (0.5N- $\text{H}_2\text{SO}_4$ , in aq.  $\text{EtOH}$ ) 6-methylglucose, m.p. 144—145° [osazone, m.p. 186—187°; tetra(azobenzoate), m.p. 141—143°,  $[\alpha]_D^{20} + 180^\circ$  in  $\text{CHCl}_3$ ], and is reduced ( $\text{Pd}\cdot\text{C}$ ,  $\text{H}_2$ ) to 6-methyl-1 : 2-isopropylidene-glucosulphate, m.p. 71°, which, with  $\text{KOH}$  and  $\text{CH}_2\text{PhCl}$ , gives 3 : 5-dibenzyl-6-methyl-1 : 2-isopropylidene-glucosulphate, b.p. 208—211°/0.05 mm., m.p. 39—41°,  $[\alpha]_D^{20} - 40.56^\circ$  in  $\text{CHCl}_3$ . Methanolysis affords 3 : 5-dibenzyl-6-methyl-( $\alpha + \beta$ )-methylglucosulphate, b.p. 185—192°/0.05 mm.,  $[\alpha]_D^{20} - 30.9^\circ$ , further methylated ( $\text{Me}_2\text{SO}_4$ ,  $\text{KOH}$ ) to 3 : 5-dibenzyl-2 : 6-dimethyl-( $\alpha + \beta$ )-methylglucosulphate, b.p. 203—207°/0.01 mm.,  $[\alpha]_D^{20} - 21.05^\circ$  in  $\text{CHCl}_3$ , which is hydrogenated ( $\text{Pd}\cdot\text{C}$ ) to 2 : 6-dimethyl-( $\alpha + \beta$ )-methylglucosulphate (V), b.p. 118—120°/0.05 mm.,  $[\alpha]_D^{20} + 5.17^\circ$  in  $\text{CHCl}_3$ , converted into the equilibrium pyranoside mixture, b.p. 130°/0.01 mm.,  $[\alpha]_D^{20} + 0.37^\circ$  in  $\text{CHCl}_3$ , with  $\text{MeOH}\cdot\text{HCl}$ . (V) is hydrolysed by aq.  $\text{HCl}$  to 2 : 6-dimethylglucose,  $[\alpha]_D^{20} + 59.8^\circ \rightarrow + 63.3^\circ$ , which affords 6-methylglucosazone with  $\text{NHPh}\cdot\text{NH}_2$ . 2 : 6-Dimethylglucose 1 : 3 : 4-trisazobenzoate exists in two forms, m.p. 205—207°,  $[\alpha]_D^{20} - 275^\circ$  in  $\text{CHCl}_3$ , and (more sol.) m.p. 128—131°,  $[\alpha]_D^{20} - 172^\circ$  in  $\text{CHCl}_3$ . 2 : 3 : 4-Trimethylglucose 1 : 6-bisazobenzoate has m.p. 133° (cf. A., 1943, II, 255).

J. WA.

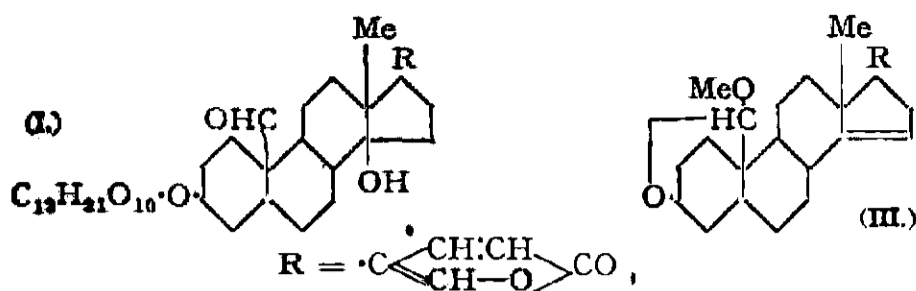
**Chemistry of sulphite cooking. XLI. Effect of sulphite-cooking acids on different types of sugars.** Fermentation of sulphite liquors of diverse origins. E. Hägglund, H. Heiwinkel, and T. Bergek (*J. pr. Chem.*, 1943, [ii], 162, 2—18).—Heating fructose in  $\text{H}_2\text{O}$  containing  $\text{CaO}$  (1.2%) and  $\text{SO}_2$  (4.43%) at 75°, removing polythio-acids by  $\text{H}_2\text{SO}_4$  at 75°,  $\text{SO}_2$  in air at pH 6, and sugars by fermenting, and finally treating with  $\text{BaCO}_3$  gives a Ba salt and thence the *brucine* salt,  $\text{C}_6\text{H}_{13}\text{O}_4\cdot\text{H}_2\text{SO}_3\cdot\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2$ , m.p. 258° (corr.), of a fructose-sulphonic acid. This loses  $\text{SO}_2$  when evaporated in  $\text{H}_2\text{O}$  or slowly when heated (not cold) in 2N- $\text{NaOH}$  or 10—15%  $\text{H}_2\text{SO}_4$ , and does not reduce Fehling's solution. It is probably a rearrangement product of the primary unstable additive product. Small amounts of sugar-sulphonic acids (A) are present in sulphite liquor prepared at low pH, but in less acid solutions are converted by hydrolysis and oxidation into aldonic acids. The stability of the additive product of glucose and  $\text{SO}_2$  is a max. at pH 6.6, decomp. becoming very rapid particularly at higher pH. (A) are not fermentable and hardly affect the fermentation of glucose. The unstable sugar- $\text{SO}_2$  products of sulphite liquor are also not fermentable but strongly decelerate the fermentation of glucose. Acidic liquors yield a sugar-sulphonic acid with a low Cu no. which is greatly increased after hydrolysis; a more alkaline liquor gives different acids for which the change in Cu no. is much less. Prior treatment of sulphite liquor with alkali increases the fermentation 7—10 times by destruction of the labile additive products.

R. S. C.

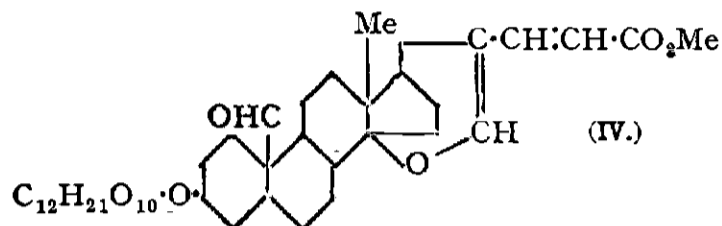
**Effects of high pressure on the inversion of sucrose and the mutarotation of glucose.**—See A., 1943, III, 683.

**Hellebrin, a crystallised glycoside from *Helleboris niger* root.** W. Karrer (*Helv. Chim. Acta*, 1943, 26, 1353—1367).—The drug is defatted with  $\text{Et}_2\text{O}$  and extracted with  $\text{H}_2\text{O}$ . The aq. extract is treated successively by  $\text{Pb}(\text{OAc})_2$  and  $\text{Na}_2\text{HPO}_4$  after which the glycoside is adsorbed on C. The adsorbate is extracted with  $\text{MeOH}\cdot\text{CH}_2\text{Cl}_2$ , and the residue from this extract is treated with abs.  $\text{EtOH}$ , thereby giving crude hellebrin (I),  $\text{C}_{36}\text{H}_{52}\text{O}_{15}$ , best cryst. from  $\text{MeOH}$ . It has m.p. 283—284°,  $[\alpha]_D^{20} - 23.4^\circ \pm 0.2^\circ$  in 50%  $\text{MeOH}$ . (I) gives a red colour in conc.  $\text{H}_2\text{SO}_4$  and a blue to green Liebermann cholesterol reaction. It does not give the Legal test or the Baljet reaction, thus indicating the presence of a 6- rather than a 5-membered lactone ring. This probability is confirmed by the close similarity of the absorption spectra of (I), scillaren A, and bufagin. The negative reaction of (I) with  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  indicates the absence of a double linking in the hydrophenanthrene ring system. Physiologically (I) is second only to convallatoxin (II) in cardiac activity. (I) is not

converted into a cryst. genin by boiling aq. or aq. alcoholic  $\text{H}_2\text{SO}_4$ ; the sugar component is glucose. When kept in 2.5%  $\text{HCl-MeOH}$



at  $38^\circ$  for several days (I) affords  $\alpha$ -methyl- $D$ -glucoside and a compound (III), m.p.  $\sim 206^\circ$ , which contains 1 OMe but no active H. The ready methylation indicates the presence of CHO as in (II),  $k$ -strophanthin, and  $\beta$ -antiarin; the action of the acid leads to loss of sugar and 1  $\text{H}_2\text{O}$  and production of a cyclosemiacetal with simultaneous etherification of the OH of the acetal. This behaviour considered in conjunction with the constitution of the known cardiac



glucosides suggests the structures (I) and (II).  $\text{KOH-MeOH}$  at  $0^\circ$  and subsequently at room temp. transforms (I) into *Me isohellebrinate*,  $\text{C}_{37}\text{H}_{54}\text{O}_{15}$ , decomp.  $\sim 230^\circ$ , softens at  $195-200^\circ$ , which has very little cardiac activity. (I) and boiling  $\text{Ac}_2\text{O-NaOAc}$  give *hellebrin hepta-acetate*, m.p. (indef.)  $159-165^\circ$ , in which all the Ac residues are in the sugar component.

H. W.

**Chemical nature of vitamin-P.**—See A., 1943, III, 579.

**Limit dextrins and starch. V. Fermentability of starch breakdown-products.**—See A., 1943, III, 684.

**Enzymic degradation of starch. Structure of starch molecules.** K. Myrbäck (*J. pr. Chem.*, 1943, [ii], 162, 29—62).—A lecture. Starch is a much-branched chain mol. Enzymes degrade all the straight-chain parts until they meet a P substituent, a branch, or an isomaltose linking. Limit dextrins contain these "abnormal" portions. Enzymes first anchor themselves to the non-reducing end of the chain and attack the sixth unit (which is near in space) and so lead often to many six-unit dextrins or six-membered rings.

R. S. C.

**Micellar theory of cellulose.** T. Lieser (*Ber.*, 1941, 74, [B], 708—714).—In reply to Staudinger (A., 1938, II, 45) it is pointed out that the results of recent work (which is reviewed) make it clear that the majority of the reactions of cellulose and its derivatives are micellar, not macromol., in character. When by special methods the micelles are themselves dispersed as macromols., all the functional groups are reactive, whereas normally those in the interior of the micelles do not react since they are inaccessible.

F. L. U.

**Fine structure of cellulose fibre.**—See A., 1943, I, 300.

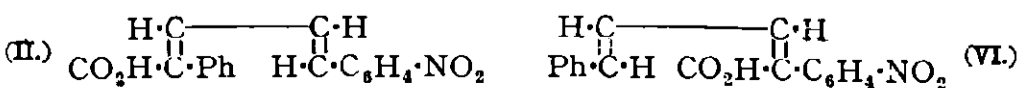
**Electron-microscopic investigation of degradation of cellulose fibres.**—See B., 1943, II, 345.

### III.—HOMOCYCLIC.

**Demjanoff's reaction for the enlargement of rings.** Y. R. Naves and P. Bachmann (*Helv. Chim. Acta*, 1943, 26, 1334—1337; cf. Demjanoff *et al.*, A., 1903, i, 403).—The hydrocarbon fraction which accompanies cyclocitronellol and the trimethylcycloheptanols when Demjanoff's reaction is applied to dihydrocyclogeranylamine contains 2-methylene-1:1:3-trimethylcyclohexane in addition to 1:1:4-trimethylcycloheptene.

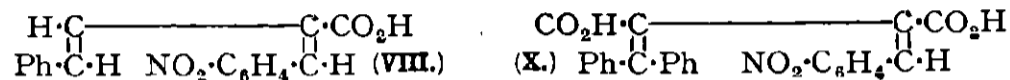
H. W.

**Attempted synthesis of a cyclooctatetraene. cis-trans-Isomerism of substituted di- and tri-phenylbutadienes.** G. B. Bachman and R. I. Hoaglin (*J. Org. Chem.*, 1943, 8, 300—315).—Attempts to prepare cyclooctatetraene (I) by a Pschorr-type synthesis from  $\text{CHPh:CH:CH:CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot o$  (A) failed. Reactivity of (I) is expected because inability to assume a planar form prevents its having a high resonance energy. cycloDecapentadiene should be more "benzenoid" since it can assume the planar form annexed. Three steric forms of (A) or its derivatives are synthesised. Structures assigned below are based mainly on analogy. *cis-trans- $\alpha$ -Phenyl- $\delta$ -o-nitrophenylpentadienoic acid* (II), m.p.  $208-209^\circ$ , is obtained



(80—85%) from  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:CH:CHO}$  (III),  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$ , (80—85%) from  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:CH:CHO}$  (III),  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ , (III),  $\text{PbO}$ , and  $\text{Ac}_2\text{O}$

at  $140-145^\circ$ . It is converted by Cu chromite in quinoline at  $210-220^\circ$  into *cis-trans- $\alpha$ -phenyl- $\delta$ -o-nitrophenylbutadiene* (IV) (75%), m.p.  $79-80^\circ$ , and is reduced by boiling  $\text{FeSO}_4\cdot\text{NH}_3\cdot\text{H}_2\text{O}$  to *cis-trans- $\alpha$ -phenyl- $\delta$ -o-aminophenylpentadienoic acid* (85—90%), m.p.  $202-203^\circ$ , which by decarboxylation affords *cis-trans- $\alpha$ -phenyl- $\delta$ -o-aminophenylbutadiene* (V), an oil (hydrochloride, softens  $195^\circ$ , decomp.  $210-215^\circ$ ).  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$  [best (55%) obtained from  $\text{CH}_2\text{Ar}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  by  $\text{H}_2\text{O}_2$ ], (III), and  $\text{Ac}_2\text{O}$  at  $110-120^\circ$  give *trans-trans- $\delta$ -phenyl- $\alpha$ -o-nitrophenylpentadienoic acid* (VI) (23.5%), m.p.  $203-204^\circ$ , converted by Cu chromite in quinoline into *trans-trans- $\alpha$ -phenyl- $\delta$ -o-nitrophenylbutadiene* (VII), m.p.  $98-99^\circ$ , which is also obtained from (IV) by a trace of I in boiling  $\text{PhNO}_2$  and in 10% yield by treating  $\text{CHPh:CH:CH:CH}\cdot\text{CO}_2\text{H}$  in  $\text{COMe}_2$  with  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  in aq.  $\text{HCl}$  and treating the product with aq.  $\text{CuCl}_2\cdot\text{NaOAc}$ .  $\text{FeSO}_4\cdot\text{NH}_3$  reduces (VII) to *trans-trans- $\alpha$ -phenyl- $\delta$ -o-aminophenylbutadiene*, m.p.  $132-133^\circ$  (hydrochloride, decomp.  $224-226^\circ$ ), which is also obtained from (V) by boiling dil.  $\text{H}_2\text{SO}_4$ . *trans-cis- $\gamma$ -Phenyl- $\alpha$ -o-nitrobenzylidene- $\Delta^3$ -butenoic acid* (VIII), m.p.  $187-188^\circ$ , is obtained (17%) from  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  (IX),  $\text{CHPh:CH:CH}_2\cdot\text{CO}_2\text{Na}$ , and  $\text{Ac}_2\text{O}$  at  $100^\circ$  or (64%) from  $\text{CHPh:CH:CH}_2\cdot\text{CO}_2\text{H}$  (IX),  $\text{PbO}$ , and  $\text{Ac}_2\text{O}$ ; with  $\text{FeSO}_4\cdot\text{NH}_3$  it gives the lactam, m.p.  $257-258^\circ$ , of *trans-trans- $\gamma$ -phenyl- $\alpha$ -o-amino-benzylidene- $\Delta^3$ -butenoic acid*. The *cis*-acid (X), m.p. (solvent-free)



$237-238^\circ$  (decomp.) (improved prep.; cf. Stobbe *et al.*, A., 1906, i, 91), with  $\text{FeSO}_4\cdot\text{NH}_3$  gives the amorphous *cis-NH<sub>2</sub>-acid* (XI) (hydrochloride, decomp.  $276-278^\circ$ ) (*loc. cit.*), but with a trace of I in boiling  $\text{PhNO}_2$  gives an *anhydride* (XII), m.p.  $256-257^\circ$ , hydrolysed by alkali to an *isomeride*,  $+\text{H}_2\text{O}$ , of (X) which after softening at  $\sim 130^\circ$  re-forms (XII). Attempts to cyclise (XII) failed.

R. S. C.

**Number of structural isomerides in simple ring compounds. II.** T. L. Hill (*J. Physical Chem.*, 1943, 47, 413—421).—Mathematical. Equations permitting the calculation of the no. of structural isomerides in a simple symmetrical ring of  $n$  members for any val. of  $n$  and for any kind of substitution have been derived (cf. A., 1943, II, 296).

C. R. H.

**New benzene substitution rule.** G. N. Copley (*Ind. Chem.*, 1943, 19, 505—510).—If X be the atom attached to the  $\text{C}_6\text{H}_6$  nucleus in a compound  $\text{C}_6\text{H}_5\text{XY}$  then the group Y which contains X is an *o-p*-directing group when the valency of X is  $\geq 4$  and a *m*-directing group when the valency of X is  $\leq 4$ . Although the rule holds good in nearly all cases where the valency is taken to be the ordinary classical valency of the atom in question it is more satisfactory to determine the valency by the four-bond max. rule, which is discussed in detail; it is then in complete accord with the electronic theory.

H. W.

**Alkylation of aromatic hydrocarbons.**—See B., 1943, II, 309.

**Physical data of *p*-alkyltoluenes.**—See A., 1943, I, 300.

**Scission of alkyl groups in the Friedel-Crafts reaction.** J. von Braun and O. Schattner (*Ber.*, 1941, 74, [B], 22—26).—When the chlorides of dialkylacetic acids ( $\text{CHR}_2\cdot\text{COCl}$ ) react (Friedel-Crafts) with  $\text{C}_6\text{H}_6$  there are formed, in addition to  $\text{COPh}\cdot\text{CHR}_2$ , higher-boiling homologues containing a group R in the *p*-position since oxidation yields *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$  (I).  $n\text{-C}_{10}\text{H}_{21}\text{Br}$  condensed with  $n\text{-C}_{10}\text{H}_{21}\cdot\text{CH}(\text{CO}_2\text{Et})_2$  gives *Et<sub>2</sub> didecylmalonate*, b.p.  $196-198^\circ/0.2$  mm., which is hydrolysed (alkali) and decarboxylated to give *di-n-decylacetic acid*, m.p.  $54^\circ$  (*Me* ester, b.p.  $218-222^\circ/13$  mm., m.p.  $26^\circ$ ). The chloride, b.p.  $240-242^\circ$ , with  $\text{AlCl}_3$  and  $\text{C}_6\text{H}_6$  (standardised conditions) affords mainly  *$\omega$ -di-n-decylacetophenone* (II), b.p.  $218-220^\circ/0.3$  mm., and a small quantity of an oil,  $\text{C}_{38}\text{H}_{78}\text{O}$ , b.p.  $290-300^\circ/0.3$  mm., oxidised by  $\text{HNO}_3$  to (I). (II) gives no cryst. derivatives and is reduced ( $\text{Ni}, \text{H}_2$ ) to  *$\beta$ -decyldodecylbenzene* [ *$\beta\beta$ -didecylethylbenzene*], b.p.  $218-222^\circ/0.7$  mm. Diheptylacetic acid, m.p.  $28^\circ$ , b.p.  $200^\circ/13$  mm., is conveniently obtained from  $(\text{C}_7\text{H}_{15})_2\text{C}(\text{CO}_2\text{Et})_2$ , b.p.  $200^\circ/13$  mm.; the chloride, b.p.  $178-180^\circ/14$  mm.,  $\text{C}_6\text{H}_6$ , and  $\text{AlCl}_3$  give *diheptylacetophenone*, b.p.  $224-228^\circ/12$  mm., reduced (Clemmensen) to  *$\beta$ -heptylnonylbenzene* [ *$\beta\beta$ -diheptylethylbenzene*], b.p.  $203-205^\circ/14$  mm., and an oil  $\text{C}_{29}\text{H}_{58}\text{O}$  [*heptyl-phenyl  $\alpha$ -heptyloctyl ketone*], b.p.  $270-274^\circ/0.5$  mm., oxidised ( $\text{HNO}_3$ ) to (I). Diisoamylacetyl chloride, b.p.  $106^\circ/12$  mm.,  $\text{C}_6\text{H}_6$ , and  $\text{AlCl}_3$  give  *$\omega$ -diisoamylacetophenone*, b.p.  $172-176^\circ/12$  mm., reduced (Clemmensen) to  *$\epsilon$ -methyl- $\beta$ -isoamylhexylbenzene*, b.p.  $145-150^\circ/11$  mm., and a compound,  $\text{C}_{23}\text{H}_{46}\text{O}$ , b.p.  $216-218^\circ/0.3$  mm.  $\text{Pr}^i\text{COCl}$  gives *isobutyrophenone*, b.p.  $210-230^\circ$ , as sole product. *iso-C<sub>5</sub>H<sub>11</sub>·CHMe·COCl* affords *methylisoamylacetophenone*, b.p.  $152-154^\circ/16$  mm., and a substance,  $\text{C}_{19}\text{H}_{38}\text{O}$ , b.p.  $180-220^\circ/0.2$  mm.  *$\beta\beta$ -Diisoamylethyl bromide* and  $\text{KCN}$  give 100% of (*iso-C<sub>5</sub>H<sub>11</sub>·CH·CH<sub>2</sub>·CN*), b.p.  $126^\circ/11$  mm., hydrolysed to the acid, b.p.  $161-163^\circ/11$  mm., via the amide, m.p.  $91^\circ$ ; the chloride, b.p.  $120-125^\circ/13$  mm.,  $\text{C}_6\text{H}_6$ , and  $\text{AlCl}_3$  give exclusively  *$\beta\beta$ -diisoamylpropio-phenone*, b.p.  $190-195^\circ/13$  mm.

J. WA.

**Diene synthesis with  $\beta$ -nitrostyrene.** C. F. H. Allen, A. Bell, and J. W. Gates, jun. (*J. Org. Chem.*, 1943, 8, 373—379).— $\text{CHPh:CH}\cdot\text{NO}_2$

(I) reacts readily with dienes (cf. A., 1937, 11, 147). With  $(\text{CH}_2\text{:CH})_2$  in PhMe at  $150^\circ$ , isoprene at  $70-80^\circ$ ,  $(\text{CH}_2\text{:CMe})_2$  at  $100^\circ$ ,  $(\text{CHPh:CH})_2$  or  $(\text{CH}_2\text{:CPh})_2$  in  $o\text{-C}_6\text{H}_4\text{Cl}_2$ , (I) gives 1-nitro-2-phenyl- (II) (70%), m.p.  $103^\circ$ , 1-nitro-2-phenyl-4- or -5-methyl- (58%), m.p.  $52^\circ$ , 1-nitro-2-phenyl-4:5-dimethyl- (III) (82%), m.p.  $96^\circ$ , 1-nitro-2:3:6-triphenyl- (IV), m.p.  $130^\circ$  (with N oxides and a product, m.p.  $76^\circ$ ), or 1-nitro-2:4:5-triphenyl- $\Delta^4$ -cyclohexene (9%), m.p.  $175^\circ$ , respectively. With cyclo-hexa- or -penta-diene, (I) gives 1-nitro-2-phenyl-3:6-endo-methylene- (100%), b.p.  $145^\circ/1\text{ mm.}$ , and -ethylene- $\Delta^4$ -cyclohexene (25%), b.p.  $138-142^\circ/1\text{ mm.}$ , respectively. With phellandrene, it gives a product,  $\text{C}_{18}\text{H}_{23}\text{O}_2\text{N}$  (25%), m.p.  $85^\circ$ , b.p.  $195^\circ/1\text{ mm.}$  With tetraphenylcyclopentadienone in  $\text{C}_6\text{H}_5\text{Cl}_3$  (no reaction in absence of a solvent), (I) gives  $\text{C}_6\text{HPh}_5$ , CO, and N oxides. With 10-methylene-9-anthrone in boiling AcOH, (I) gives N oxides, 3-phenylbenzanthrone-7-one, and 2-nitro-3-phenyl-1:2:3:3a-tetrahydrobenzanthrone-7-one (3%), m.p.  $255^\circ$  (oxidised by  $\text{CrO}_3\text{-AcOH}$  to 1-benzoylanthraquinone). With 1:2-diphenyl- or 1:2-diphenyl-4:5-dimethyl-isobenzofuran in boiling EtOH, (I) gives 3-nitro-1:4-epoxy-1:2:4-triphenyl-1:2:3:4- (V) (100%), m.p.  $163^\circ$ , and -1:2:4-triphenyl-6:7-dimethyl-1:2:3:4-tetrahydronaphthalene (VI) (100%), m.p.  $182^\circ$ , respectively. Furan, sylvan, and 2:5-dimethylfuran do not react with (I) at  $100^\circ$  or in a sealed tube. Br converts (II) or (III) in cold  $\text{CHCl}_3$  into 4:5-dibromo-1-nitro-2-phenyl-cyclohexane, m.p.  $107^\circ$ , and -4:5-dimethylcyclohexane, m.p.  $69^\circ$ , respectively, but (IV) gives only  $(\text{CHPhBr}\cdot\text{CHBr})_2$ . The K (? Na) salt of (III) with Br-EtOH gives 1-bromo-1-nitro-2-phenyl-4:5-dimethyl- $\Delta^4$ -cyclohexene, m.p.  $68-69^\circ$ , which decomposes explosively if heated alone or regularly in *p*-cymene at  $100-165^\circ$ , or violently if distilled at 3 mm. Hydrogenation (Raney Ni; EtOH) of (II) or (III) gives 2-phenyl- (hydrochloride, m.p.  $>220^\circ$ ) or 2-phenyl-4:5-dimethyl- $\Delta^4$ -cyclohexenylamine, b.p.  $129-132^\circ/3\text{ mm.}$  [hydrochloride, m.p.  $173^\circ$  (decomp.)], respectively. 30-32% HBr-AcOH at room temp. and then the b.p. dehydrates (V) or (VI) to 3-nitro-1:2:4-triphenyl-, m.p.  $218-219^\circ$ , or -1:2:4-triphenyl-6:7-dimethyl-naphthalene, m.p.  $237-238^\circ$ , respectively, reduced by Zn dust in AcOH to 1:3:4-triphenyl-, m.p.  $256-257^\circ$ , and 1:3:4-triphenyl-6:7-dimethyl-2-naphthylamine, m.p.  $226-227^\circ$ , respectively, which by treatment with, successively,  $\text{OBu}\cdot\text{NO-AcOH-EtOH}$  at  $0^\circ$ ,  $\text{HCl-AcOH}$  at  $0^\circ$ , and boiling EtOH give 1:2:4- $\text{C}_{10}\text{H}_5\text{Ph}_3$  (VII) (A., 1929, 681) and 1:2:4-triphenyl-6:7-dimethylnaphthalene (VIII), m.p.  $167-168^\circ$ , respectively. Styrene with isobenzofuran or its 4:5-Me<sub>2</sub> derivative in boiling xylene give 1:4-epoxy-1:2:3-triphenyl-, m.p.  $116-117^\circ$ , and -1:2:3-triphenyl-6:7-dimethyl-1:2:3:4-tetrahydronaphthalene, m.p.  $172-173^\circ$ , and thence (HBr-AcOH) (VII) and (VIII), respectively. R. S. C.

**Alkyl-oxygen fission in sulphinic ethers.** M. P. Balfe, J. Kenyon, and A. L. Tárnoky (J.C.S., 1943, 446; cf. A., 1943, II, 9).—Alkyl-O fission in sulphinic esters may occur analogously to the case of carboxylic esters. The racemising alkyl-O fission is promoted by the electron-release of an aromatic substituent in the alkyl group. Rearrangement of (–)-phenylmethylcarbinyl *dl*-*p*-toluenesulphonate to *dl*-*p*-tolyl  $\alpha$ -phenylethyl sulphone involves alkyl-O fission. Other examples are discussed. A. T. P.

**Magnetic investigations of organic substances. XX. True carbon radical with para "free valencies."** E. Müller and E. Tietz (Ber., 1941, 74, [B], 807-824).—4:3:5:1-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>·CO<sub>2</sub>H, m.p.  $291^\circ$  (obtained in 15% yield from *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and  $\text{KClO}_2$  in  $\text{AcOH-NaOAc-conc. HCl}$ ), gives  $(\text{CH}_2\text{N}_2\text{-COMe}_2)$  the Me ester (I), m.p.  $82^\circ$ , converted (Sandmeyer) into Me 3:5-dichloro-4-iodobenzoate, m.p.  $98^\circ$ . This with "Naturkupper C" (previously heated in  $\text{N}_2$ ) at  $280^\circ$  affords Me<sub>2</sub> 2:6:2':6'-tetrachlorodiphenyl-4:4'-dicarboxylate (II), m.p.  $152^\circ$ , which with *p*-LiC<sub>6</sub>H<sub>4</sub>Ph in  $\text{C}_6\text{H}_6$  yields 2:6:2':6'-tetrachloro-4:4'-di(hydroxydi-*p*-diphenylmethyl)diphenyl (III), m.p.  $248-249^\circ$  (deep blue halochromism with conc.  $\text{H}_2\text{SO}_4$ ), obtained with difficulty from admixed resinous products.  $\text{SOCl}_2$  and (III) in  $\text{C}_6\text{H}_6$  give the 4:4'-di(chlorodi-*p*-diphenylmethyl) derivative, m.p.  $295-296^\circ$ , converted by Cu or "mol." Ag in  $\text{C}_6\text{H}_6$  and  $\text{N}_2$  into a dark brown solution (layers  $>3\text{ mm.}$  are non-transparent) of 2:6:2':6'-tetrachloro-4:4'-di-*p*-diphenylmethylmethylidiphenyl (IV). The solution is decolorised rapidly by air giving a diperoxide, bright yellow, m.p.  $155-156^\circ$ , which does not liberate I from acidified KI. Solid (IV), m.p.  $180-182^\circ$ , is diamagnetic and is considered not to possess any diradical character. Solutions are paramagnetic; the diradical content of a 1.9% solution in  $\text{C}_6\text{H}_6$  is computed to be  $73\pm 7\%$  at  $20^\circ$ , and  $80\pm 8\%$  at  $80^\circ$ . Comparison of the absorption spectra of (II) and Me 3:5-dichlorobenzoate, m.p.  $58^\circ$  [by decamination of (I)], and of  $(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me-}p)_2$  and MeOBz shows that for each pair the difference is largely in the height of the extinction. 2:6:2':6'-Tetrachloro-4:4'-dibenzoyldiphenyl and *p*-LiC<sub>6</sub>H<sub>4</sub>Ph give a non-cryst. dicarbinol (blue-red halochromism with conc.  $\text{H}_2\text{SO}_4$ ), which with  $\text{SOCl}_2\text{-C}_6\text{H}_6$  affords 2:6:2':6'-tetrachloro-4:4'-di(phenyl-*p*-diphenylmethylchloromethyl)diphenyl, m.p.  $272-273^\circ$ . This is converted by Hg, Cu, or Ag in  $\text{C}_6\text{H}_6$  into 2:6:2':6'-tetrachloro-4:4'-di(phenyl-*p*-diphenylmethyl)diphenyl (V) (A., 1940, II, 302). The red-brown solution contains the diradical, the amount of which decreases with increased concn.; the corresponding peroxide has m.p.  $177-179^\circ$ . Reply is made to Theilacker *et al.* (A., 1940, II, 270),

who doubts the correctness of the conception of compounds of the type of (IV) and (V) as "doubled"  $\text{CAR}_3$ . H. B.

**Rates of dissociation of penta-arylethanes.** W. E. Bachmann, R. Hoffman, and F. Whitehead (J. Org. Chem., 1943, 8, 320-330).—Rates of dissociation of  $\text{C}_2\text{HAr}_5$  in  $o\text{-C}_6\text{H}_4\text{Cl}_2\text{-C}_5\text{H}_5\text{N-EtOH}$  at  $80^\circ$ , determined by  $\text{I-C}_5\text{H}_5\text{N-EtOH}$  (A., 1940, II, 122), are given as half-lives in min. in parentheses below.  $\text{CPh}_2\text{ArNa}$  and  $\text{CHPh}_2\text{Br}$  in  $\text{C}_6\text{H}_6$  give  $\alpha\alpha\beta\beta$ -tetraphenyl- $\alpha$ -2-, m.p.  $167-168^\circ$  (decomp. in air),  $190-202^\circ$  (decomp. in  $\text{N}_2$ ) (54.2), - $\alpha$ -3-, m.p.  $183-188^\circ$  (decomp. in air),  $196-198^\circ$  (decomp. in  $\text{N}_2$ ) (50.3), and - $\alpha$ -9-phenanthrylethane, m.p.  $149-152^\circ$  (decomp. in air),  $152-155^\circ$  (decomp. in  $\text{N}_2$ ) (5.7).  $\text{CPh}_2\text{ArCl}$ ,  $\text{CHPh}_2\text{Br}$ , and Hg in  $\text{Et}_2\text{O-C}_6\text{H}_6\text{-N}_2$  give  $\alpha\alpha\beta\beta$ -tetraphenyl- $\alpha$ -1-phenanthryl-, m.p.  $123-134^\circ$  (decomp. in air),  $125-135^\circ$  (decomp.; vac.) (0.45), and -2-fluorenyl-ethane, m.p.  $168-176^\circ$  (decomp. in air),  $187-190^\circ$  (decomp. in  $\text{N}_2$ ) (24.4), reduced by red  $\text{P-I-H}_2\text{O-AcOH-N}_2$  to diphenyl-2-fluorenylmethane (I), m.p.  $147-148^\circ$ , and converted by  $\text{I-C}_6\text{H}_6\text{-EtOH-C}_5\text{H}_5\text{N}$  at  $100^\circ$  into  $\text{C}_5\text{H}_5\text{N,CHPh}_2\text{I}$  and diphenyl-2-fluorenylcarbinol Et ether (II), m.p.  $115^\circ$ .  $\text{MgPhBr}$  and 2-benzoylfluorene in  $\text{Et}_2\text{O-C}_6\text{H}_6$  give diphenyl-2-fluorenylcarbinol (III), m.p.  $143-144^\circ$ , converted by  $\text{AcCl-C}_6\text{H}_6$  or  $\text{HCl-C}_6\text{H}_6\text{-CaCl}_2$  into the chloride, m.p.  $114-115^\circ$ , which with  $\text{Hg-C}_6\text{H}_6\text{-N}_2$  and then air gives the peroxide, m.p.  $172-173^\circ$ . With  $\text{H}_2\text{SO}_4\text{-EtOH}$ , (III) gives its Et ether (II) and with  $\text{H}_2\text{SO}_4\text{-MeOH}$  gives its Me ether (IV), m.p.  $108-109^\circ$ , converted by 45% Na-Hg in  $\text{Et}_2\text{O-N}_2$  and then EtOH and  $\text{H}_2\text{O}$  into (I). Na reacts with  $\text{C}_{10}$  of the fluorene nucleus of (I), since the product obtained therefrom by MeI is 2-benzhydryl-9-methylfluorene, m.p.  $119-120^\circ$ , which is also obtained by treating the Na derivative of (IV) with MeI and by treating 9-methylfluorene with  $\text{BzCl-AlCl}_3\text{-CS}_2$ , boiling the product with  $\text{MgPhBr-C}_6\text{H}_6$ , and reducing the carbinol thus obtained by red  $\text{P-I-H}_2\text{O-AcOH}$ .  $\text{CHPhArBr}$  (prep. from  $\text{CHPhAr-OH}$  by  $\text{AcBr}$ ) with  $\text{CPh}_3\text{Na}$  gives  $\alpha\alpha\beta\beta$ -tetraphenyl- $\beta$ -1-, m.p.  $174-180^\circ$  (decomp. in air),  $178-182^\circ$  (decomp. in  $\text{N}_2$ ) (12.4), -2-, m.p.  $145-155^\circ$  (decomp. in air),  $153-157^\circ$  (decomp. in  $\text{N}_2$ ) (32.8), and -3-phenanthryl-, m.p.  $162-174^\circ$  (decomp. in air),  $174-178^\circ$  (decomp. in  $\text{N}_2$ ) (36.1), - $\beta$ -2-naphthyl-, m.p.  $157-158^\circ$  (decomp. in air),  $177-181^\circ$  (decomp. in  $\text{N}_2$ ) (24.9), - $\beta$ -o-, m.p.  $138-144^\circ$  (decomp. in air),  $146-147^\circ$  (decomp.; vac.) (63.2), - $\beta$ -m-, m.p.  $149-153^\circ$  (decomp. in air),  $168-170^\circ$  (decomp.; vac.) (54.2), and - $\beta$ -p-fluorophenyl-, m.p.  $150-155^\circ$  (decomp. in air),  $156-157.5^\circ$  (decomp.; vac.) (66.6), - $\beta$ -o-, m.p.  $139-147^\circ$  (decomp. in air),  $170.5-171^\circ$  (decomp.; vac.) (22.2), and - $\beta$ -m-tolyl-, m.p.  $149-157^\circ$  (decomp. in air),  $157-159^\circ$  (decomp.; vac.) (41.1), - $\beta$ -o-, m.p.  $141-152^\circ$  (decomp. in air),  $165-166^\circ$  (decomp.; vac.) (20.2), and - $\beta$ -m-anisyl-, m.p.  $139-142.5^\circ$  (decomp. in air),  $144-144.5^\circ$  (decomp.; vac.) (39.6), - $\beta$ -m-, m.p.  $146-153^\circ$  (decomp. in air),  $168-169^\circ$  (decomp.; vac.) (62.8), and - $\beta$ -o-diphenyl-ethyl-ethane, m.p.  $167-173^\circ$  (decomp. in air),  $175-178^\circ$  (decomp.; vac.) (10.8). 2-C<sub>10</sub>H<sub>7</sub>·CHPh·OH (prep. from 2-C<sub>10</sub>H<sub>7</sub>·CHO and  $\text{MgPhBr}$ ) with  $\text{AcBr-C}_6\text{H}_6$  gives  $\alpha$ -2-naphthylbenzyl bromide, m.p.  $74-75^\circ$ .  $o\text{-C}_6\text{H}_4\text{F}\cdot\text{COPh}$  with  $\text{Al(OPr}^i)_3\text{-Pr}^i\text{OH}$  gives  $o$ -fluorobenzhydryl, m.p.  $41-42^\circ$ , and thence the bromide, b.p.  $172-178^\circ/17\text{ mm.}$   $\text{PhCHO}$  and  $m\text{-C}_6\text{H}_4\text{F}\cdot\text{MgBr}$  give *m*-fluorobenzhydryl, m.p.  $26-27^\circ$ , b.p.  $178-179^\circ/16\text{ mm.}$ , and thence the bromide, b.p.  $192-193^\circ/28\text{ mm.}$  *p*-Bromobenzhydryl bromide, b.p.  $176-178^\circ/14\text{ mm.}$ , and  $m\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CHPh}\cdot\text{OH}$ , m.p.  $78.5-79^\circ$  (lit.  $81^\circ$ ), are also prepared. R. S. C.

**Preparation of 1:3-dinitronaphthalene.** H. H. Hodgson and S. Birtwell (J.C.S., 1943, 433).—2:4:1-C<sub>10</sub>H<sub>5</sub>(NO<sub>2</sub>)<sub>2</sub>·NH<sub>2</sub> (I) (improved prep.) is diazotised in  $\text{H}_2\text{SO}_4$  and added to  $\text{AcOH}$  (3 parts to 1 part of  $\text{H}_2\text{SO}_4$ ) at  $<20^\circ$ , followed by  $\text{Cu}_2\text{O}$  at  $5^\circ$  to  $25-30^\circ$ ; 1:3-C<sub>10</sub>H<sub>6</sub>(NO<sub>2</sub>)<sub>2</sub>, m.p.  $146-147^\circ$ , is obtained in 82% yield, and is also formed (78%) when 2:4-dinitro-*p*-toluenesulphon-1-naphthalide and  $\text{NO}\cdot\text{SO}_4\text{H-H}_2\text{SO}_4$  at  $<10^\circ$  is added to  $\text{AcOH}$  at  $<20^\circ$ , and the hydrolysed product (I) diazotised and treated with  $\text{Cu}_2\text{O}$ . A. T. P.

**Reactions catalysed by aluminium chloride. XXII. Syntheses of hydrophenanthrene derivatives.** C. D. Nenitzescu, E. Ciorănescu, and M. Maican (Ber., 1941, 74, [B], 687-693).—The mixture of unsaturated and Cl-ketones obtained from cyclohexene,  $\text{CH}_2\text{Ph}\cdot\text{COCl}$ , and  $\text{AlCl}_3$  in  $\text{PhNO}_2$  at  $0^\circ$ —room temp. is reduced ( $\text{Na-H}_2\text{O-Et}_2\text{O}$ ) to  $\alpha$ -cyclohexyl- $\beta$ -phenylethyl alcohol (I), b.p.  $170^\circ/15\text{ mm.}$ , m.p.  $56^\circ$ . *Ph* hexahydrobenzyl ketone, b.p.  $170-171^\circ/20\text{ mm.}$  (semicarbazone, m.p.  $195^\circ$ ), from  $\text{C}_6\text{H}_6$ , cyclohexylacetyl chloride (II), and  $\text{AlCl}_3$  at  $45^\circ$ , is similarly reduced to  $\beta$ -cyclohexyl- $\alpha$ -phenylethyl alcohol, b.p.  $175^\circ/20\text{ mm.}$ , which [like (I)] is converted by distillation with  $\text{P}_2\text{O}_5$  in a vac. into 1:2:3:4:9:10:11:12-octahydrophenanthrene (contains a little spiran; dehydrogenated to phenanthrene). Methylcyclohexene,  $\text{CH}_2\text{Ph}\cdot\text{COCl}$ , and  $\text{AlCl}_3$  in  $\text{PhNO}_2$  give mixed ketones (from which 2-methyl- $\Delta^1$ -cyclohexenyl  $\text{CH}_2\text{Ph}$  ketoxime, m.p.  $153^\circ$ , is obtained) reduced to  $\alpha$ -2-methylcyclohexyl- $\beta$ -phenylethyl alcohol, b.p.  $179-183^\circ/14\text{ mm.}$ , whence ( $\text{P}_2\text{O}_5$ ) 12-methyl-1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p.  $155-157^\circ/18\text{ mm.}$  2-Methyl- $\Delta^1$ -cyclohexenylacetyl chloride,  $\text{C}_6\text{H}_6$ , and  $\text{AlCl}_3$  afford 4-phenyl-2-methylcyclohexylacetic acid, b.p.  $190-192^\circ/5\text{ mm.}$ , m.p.  $98^\circ$ . *p*-Anisyl hexahydrobenzyl ketone, b.p.  $169-170^\circ/5\text{ mm.}$ , m.p.  $45^\circ$  (semicarbazone, m.p.  $186^\circ$ ) [from  $\text{PhOMe}$ , (II), and  $\text{AlCl}_3$  in  $\text{PhNO}_2$ ], is reduced to the carbinol b.p.  $169-170^\circ/5\text{ mm.}$  —

( $P_2O_5$  at 3 mm.) 7-methoxy-1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p. 135—137°/3 mm., dehydrogenation (Se) of which gives phenanthrene.  $\Delta^1$ -cyclohexenyl *p*-methoxybenzyl ketone, m.p. 112° (from *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·COCl, cyclohexene, and AlCl<sub>3</sub> in PhNO<sub>2</sub>) (semicarbazone, m.p. 136°), could not be reduced satisfactorily. cyclopentylacetyl chloride, C<sub>10</sub>H<sub>18</sub>, and AlCl<sub>3</sub> in PhNO<sub>2</sub> give  $\beta$ -C<sub>10</sub>H<sub>7</sub> cyclopentylmethyl ketone (III), b.p. 186—187°/3 mm., m.p. 61—62°, reduced (Na, aq. MeOH, Et<sub>2</sub>O) to  $\beta$ -cyclopentyl- $\alpha$ -5:6:7:8-tetrahydro-2-naphthylethyl alcohol, b.p. 199—200°/5 mm., whence ( $P_2O_5$ ) 3:4-trimethylene-1:2:3:4:5:6:7:8-octahydrophenanthrene, b.p. 172—173°/5 mm. Dehydrogenation (Se at 250°, then 360°) of this gives some 3:4-trimethylenepheneanthrene. The oxime, m.p. 120°, of (III) with AcCl-PCl<sub>5</sub> at 0° affords cyclopentylacet- $\beta$ -naphthylamide, m.p. 125°, hydrolysed [HBr (*d* 1.49)] to  $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>. H. B.

**Reactions of hydrazoic acid. II. Quantitative study of the action with substituted benzoic acids.** L. H. Briggs and J. W. Lyttleton (J.C.S., 1943, 421—425; cf. A., 1942, II, 140).—Yields % of NH<sub>2</sub>Ar formed from HN<sub>3</sub> and the following acids in the Schmidt reaction, using conc. H<sub>2</sub>SO<sub>4</sub> (POCl<sub>3</sub> is an unsatisfactory catalyst) in C<sub>2</sub>HCl<sub>3</sub> at 40°, are: BzOH 69, *m*-C<sub>6</sub>H<sub>4</sub>X·CO<sub>2</sub>H (X = Cl 75, Br 72, I 62, OH 80, OMe 77, OEt 73, NO<sub>2</sub> 63, CN 59, CO<sub>2</sub>H 57, Me 42), *o*- 80, and *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H 78, *o*- 68, and *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H 41. The rate of reaction of the substituted acids, as determined by the time of half the evolution of N<sub>2</sub>, is, in descending order of speed (*m*-series): Me > H > OEt > OMe > OH > Br > Cl > I > CO<sub>2</sub>H > CN > NO<sub>2</sub>. In general, this is in the reverse order of the strength of the acids (from dissociation const.). *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H is an exception, presumably because of an "ortho-effect." Speed of reaction depends on the character of the substituent according as this is electrophilic, *e.g.*, NO<sub>2</sub>, or nucleophilic, *e.g.*, Me. The total vol. of N<sub>2</sub> evolved and yield of amine produced do not bear a close relation, and explanations are suggested. No trace of amine is obtained when PhOMe, NPhMe<sub>2</sub>, or PhNO<sub>2</sub> is submitted to the Schmidt reaction at 40°. The mechanism of the reaction is discussed.

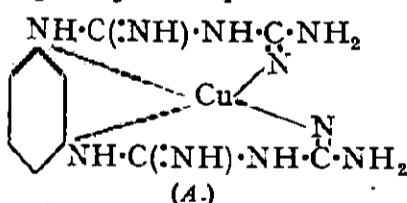
A. T. P.

**Colour and constitution. VII. Structures of mono- and dinonaphthylamines based on their visual colours. Probable constitution of 1:2-naphthaquinone.** H. H. Hodgson and H. S. Turner (J. Soc. Dyers and Col., 1943, 59, 218—220).—The NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·NH<sub>2</sub> (I) (13 known isomerides) can each resonate into one of seven quinonoid structures; since all are red except 2:1-, 3:1-, and 4:1-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·NH<sub>2</sub>, which are yellow, it is suggested that the other ten have a single linking between the central C atoms, and the above three have a double linking. By analogy, the red 1:2-O·C<sub>10</sub>H<sub>6</sub>·O should also possess a central single linking. Structures of (NO<sub>2</sub>)<sub>2</sub>C<sub>10</sub>H<sub>5</sub>·NH<sub>2</sub> are also discussed, and the effects of halogen substituents on the colours and structures of (I) are considered.

A. T. P.

**Sulphanilamide derivatives.**—See B., 1943, III, 279.

**Complex compounds of diguanide with bivalent metals. V. Copper and nickel *m*-phenylenebisdiguanidine and their salts.** P. Rây and S. K. Siddhanta (J. Indian Chem. Soc., 1943, 20, 200—203).—*m*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>·2HCl and dicyanodiamide (2 mols.) in hot H<sub>2</sub>O give *m*-phenylenebisdiguanidine hydrochloride, which with aq. NH<sub>3</sub> and aq. NH<sub>3</sub>-CuSO<sub>4</sub> affords the complex sulphate. This in aq. HCl with



KOH (excess) gives the complex base, [CuB·H<sub>2</sub><sup>+</sup>](OH)<sub>2</sub>, which forms the anhydro-base [CuB] at 110°, for which the formula (A) is suggested. The following salts are described: [CuB·H<sub>2</sub><sup>+</sup>]Cl<sub>2</sub>·1.5H<sub>2</sub>O; [CuB·H<sub>2</sub><sup>+</sup>]Br<sub>2</sub>·2H<sub>2</sub>O; [CuB·H<sub>2</sub><sup>+</sup>]I<sub>2</sub>;

[CuB·H<sub>2</sub><sup>+</sup>](NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O; [CuB·H<sub>2</sub><sup>+</sup>]SO<sub>4</sub>·0.5H<sub>2</sub>O; [CuB·H<sub>2</sub><sup>+</sup>]S<sub>2</sub>O<sub>3</sub>·2.5H<sub>2</sub>O; [CuB·H<sub>2</sub><sup>+</sup>](CNS)<sub>2</sub>·H<sub>2</sub>O. The analogous base, [NiB·H<sub>2</sub><sup>+</sup>](OH)<sub>2</sub>·2H<sub>2</sub>O {gives [NiB·H<sub>2</sub><sup>+</sup>](OH)<sub>2</sub> at 85—90° and [NiB] at 110°}, and salt, [NiB·H<sub>2</sub><sup>+</sup>]SO<sub>4</sub>·5H<sub>2</sub>O, are described; the chloride could not be prepared. S. A. M.

**Polarographic study of *cis-trans* isomerism of azo-compounds.** A. Winkel and H. Siebert (Ber., 1941, 74, [B], 670—675).—Two stages are observed in the reduction of solutions of (*m*-SO<sub>3</sub>K·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>)<sub>2</sub> at a dropping Hg cathode. Illumination of the solutions by a quartz Hg lamp causes the second stage to diminish and ultimately to disappear, whilst the consumption of H (2 atoms H per mol.) remains unaffected. The phenomenon is attributed to the presence in the original solution of *cis*- and *trans*-forms in approx. equimol. proportion, the latter being converted into the former under the influence of light. The *cis*-compound has a deeper colour than the *trans*-compound and can be conc. chromatographically to the extent of 10%, or of 25% if the Et<sub>2</sub> ester is used. The polarographic behaviour of (NPh)<sub>2</sub> in EtOH solution is similar to that of its disulphonic acid. The energy of the *cis-trans* transition, calc. from the reduction potentials, is 10.8 kg.-cal. per mol., in agreement with the val., ~12 kg.-cal., obtained from the heats of fusion. F. L. U.

**Radioactive disazo-dyes. II. Synthesis and properties of radioactive dibromo-trypan-blue and radioactive dibromo-Evans-blue.** N 2 (A., II.)

L. H. Tobin and F. D. Moore (J. clin. Invest., 1943, 22, 155—159).—*o*-Tolidine was converted into the radioactive 5:5'-Br<sub>2</sub>-derivative by means of <sup>82</sup>Br (obtained from EtBr bombarded in a cyclotron) and this was converted into the disazo-dyes as usual; the dry products have activity ~0.5  $\mu$ c. per mg. when fresh. The brominated dyes are redder in shade than the non-brominated dyes; the absorption max. was shifted by bromination from 630 to 545  $\mu$ . for Evans-blue and from 600 to 550  $\mu$ . for trypan-blue. Other properties are compared.

**Azo-compounds and their intermediates. XXV. Aminohydrazo-compounds.** P. Ruggli and K. Hölzle (Helv. Chim. Acta, 1943, 26, 1190—1197).—Partial hydrogenation (Raney Ni-EtOH at room temp.) of *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Ph (I) gives NH<sub>2</sub>Ph and *p*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>. Gradual addition of Zn dust and 35% aq. NH<sub>3</sub> to (I) in EtOH at 50—55° until the solution becomes colourless leads to 4-aminohydrazobenzene (II), m.p. 81—84° to a brown melt, becomes yellow at ~50°. (II) is very unstable and decomposes completely within a few hr. even in a high vac. It is immediately disproportionated by Ac<sub>2</sub>O but  $\beta$ -acetyl- $\alpha$ -phenyl- $\beta$ -*p*-acetamidophenylhydrazine, m.p. 198—200° (decomp.) (also +MeOH), can be obtained by reduction of (I) in C<sub>5</sub>H<sub>5</sub>N with Zn dust and a little AcOH followed by acetylation with Ac<sub>2</sub>O; hydrogenation (Raney Ni) transforms this into NH<sub>2</sub>Ph and *p*-C<sub>6</sub>H<sub>4</sub>(NHAc)<sub>2</sub>. Similarly *o*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Ph (III) is reduced to 2-aminohydrazobenzene, m.p. 94—95° (decomp.), becomes yellow at 70°, which is somewhat more stable than (II), can be preserved for 1 day in a vac., but rapidly becomes discoloured in air; reduction of (III) by Zn dust in C<sub>5</sub>H<sub>5</sub>N containing a little AcOH followed by acetylation (Ac<sub>2</sub>O) yields 2-acetamidohydrazobenzene, m.p. 167—168° (decomp.), oxidised by yellow HgO to *o*-NHAc·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Ph. *m*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Ph is reduced by NH<sub>3</sub>-H<sub>2</sub>S in EtOH to 3-aminohydrazobenzene, m.p. 107°, which is moderately stable in air when dry. 4-Amino-4'-phenylhydrazinodiphenyl, m.p. 139—141° (disproportionation), becomes pale yellow at ~100°, obtained by reduction (H<sub>2</sub>S) of the azo-compound, is moderately stable in air and gives an Ac<sub>2</sub> derivative, NHPH·NAC·C<sub>6</sub>H<sub>4</sub>·C<sub>6</sub>H<sub>4</sub>·NHAc, m.p. 232—233°, catalytically hydrogenated to NH<sub>2</sub>Ph and (C<sub>6</sub>H<sub>4</sub>·NHAc)<sub>2</sub>. H. W.

**Union of aryl nuclei. VI. Reactions with 1-aryl-3:3-dimethyltriazens.** J. Elks and D. H. Hey [with (in part) J. W. Haworth and C. W. Pritchett] (J.C.S., 1943, 441—445; cf. A., 1940, II, 238).—NMe<sub>2</sub>·N:NAr are prepared from ArN<sub>2</sub>Cl-33% aq. NHMe<sub>2</sub>-30% aq. Na<sub>2</sub>CO<sub>3</sub>. 1-Phenyl-3:3-dimethyltriazene, b.p. 125—127°/19 mm., with boiling C<sub>6</sub>H<sub>6</sub>-dry HCl gives NHMe<sub>2</sub>, PhCl, and Ph<sub>2</sub> (25%); increased to 37% in C<sub>6</sub>H<sub>6</sub>-AcOH, with PhNO<sub>2</sub> at 100° (bath) gives a mixture (35%) of *p*- (I) and *o*-C<sub>6</sub>H<sub>4</sub>Ph·NO<sub>2</sub>, and with C<sub>5</sub>H<sub>5</sub>N-HCl at 100° (bath) yields 2-, 3-, and 4-phenylpyridine (51%). 1-*p*-Nitrophenyl-3:3-dimethyltriazene, m.p. 144—145°, affords (I) (52%) with C<sub>6</sub>H<sub>6</sub>-HCl, and with C<sub>5</sub>H<sub>5</sub>N-HCl gives 50% of 2- + 3-*p*-nitrophenylpyridine; the *m*-NO<sub>2</sub>-isomeride, m.p. 99—100°, with C<sub>6</sub>H<sub>6</sub>-HCl, but not with C<sub>6</sub>H<sub>6</sub>-AcOH, yields *m*-C<sub>6</sub>H<sub>4</sub>Ph·NO<sub>2</sub> (53%). 1-*o*-Carboxyphenyl-, m.p. 124—126° (decomp.) (C<sub>6</sub>H<sub>6</sub>-HCl gives *o*-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H and no diaryl), and 1- $\beta$ -naphthyl-3:3-dimethyltriazene, m.p. 57—58°, are prepared; the latter and C<sub>6</sub>H<sub>6</sub>-AcOH yield 2-C<sub>10</sub>H<sub>7</sub>Ph (36%), and C<sub>5</sub>H<sub>5</sub>N-HCl give mixed 2-pyridyl-naphthalenes (41%) and thence isomeric picrates, m.p. 199—200° (base, m.p. 99—100°), 177—178° [base (II), m.p. 69—70°], and 216—217°.  $\beta$ -C<sub>10</sub>H<sub>7</sub>·N<sub>2</sub>Cl and C<sub>5</sub>H<sub>5</sub>N at 20—25°, and then SnCl<sub>2</sub>-HCl-AcOH, afford (II), also obtained from  $\beta$ -C<sub>10</sub>H<sub>7</sub>·NAC·NO and C<sub>5</sub>H<sub>5</sub>N. 1-5'-Quinoyl-3:3-dimethyltriazene, m.p. 30—40° (impure), with C<sub>6</sub>H<sub>6</sub>-HCl gives 5-chloroquinoline (picrate, m.p. 220—223°) and 5-phenylquinoline (13%), m.p. 82—83° (picrate, m.p. 210—211°). 1-Phenyl-3:3-dimethyltriazene-3':4'-dicarboxylimide, m.p. 251—253° (decomp.) [from 4:1:2-NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>NH (III)], and C<sub>6</sub>H<sub>6</sub>-HCl give a little 4:1:2-C<sub>6</sub>H<sub>3</sub>Ph(CO<sub>2</sub>)<sub>2</sub>NH (IV), and with C<sub>5</sub>H<sub>5</sub>N-HCl, a mixture (49%) of 4-pyridylphthalimides, m.p. 232—243°, also obtained (m.p. 238—245°) from diazotised (III) and C<sub>5</sub>H<sub>5</sub>N at 40—50°. Me<sub>2</sub> 1-phenyl-3:3-dimethyltriazene-3':4'-dicarboxylate, m.p. 74—75°, and C<sub>6</sub>H<sub>6</sub>-HCl yield 4:1:2-C<sub>6</sub>H<sub>3</sub>Ph(CO<sub>2</sub>Me)<sub>2</sub> (V) (66%). 1-*o*-Carboxymethoxyphenyl-3:3-dimethyltriazene, b.p. 180—182°/18 mm., and molten 2-C<sub>10</sub>H<sub>7</sub>·OMe-HCl or -AcOH at 100° (bath) afford 2:1-OMe·C<sub>10</sub>H<sub>6</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Me-*o* (25 or 29% respectively). Diazotised (III) and C<sub>6</sub>H<sub>6</sub>-aq. NaOAc at 5—10° give (IV), and 1:2:4-(CO<sub>2</sub>Me)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·N<sub>2</sub>Cl and C<sub>6</sub>H<sub>6</sub>-aq. NaOH or -NaOAc yield (V) (34 or 52% respectively). A. T. P.

**Production of phenol from cyclohexanol and cyclohexanone.**—See B., 1943, II, 341.

**Manufacture of phenols.**—See B., 1943, II, 341.

**Absorption spectra of *m*-substituted phenols; influence of nucleophilic substituents on electronic mobility.**—See A., 1943, I, 271.

**Mesomeric anions containing nitro-groups.**—See A., 1943, I, 295.

**Amino-acid ester salts of phenols.**—See B., 1943, II, 341.

**Peroxidic degradation of substituted aromatic aldehydes and ketones to the corresponding phenols. II. Degradation with peracetic acid.** A. von Wacek and A. von Bézard (Ber., 1941, 74, [B],

845—857).—*o*-OH·C<sub>6</sub>H<sub>4</sub>·CHO is oxidised by AcO<sub>2</sub>H [containing 0.5% of *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>H (I) unless stated otherwise] at 35—40° to muconic acid and some *o*-OH·C<sub>6</sub>H<sub>4</sub>·O·CHO (II), b.p. 125°/12 mm. (with NHPH·NH<sub>2</sub> gives ? *N*-formyl-*N*'-phenylhydrazine, m.p. 147°), readily hydrolysed to *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>. Use of Ac<sub>2</sub>O—AcO<sub>2</sub>H at 25° affords 88% of (II), which with Et<sub>2</sub>O—CH<sub>2</sub>N<sub>2</sub> gives *o*-anisyl formate, b.p. 109°/12 mm., hydrolysed to guaiacol. These results support the rearrangement mechanism (a) (A., 1943, II, 260) but do not preclude (b) direct attack by O at the C carrying CHO. That both mechanisms can operate is proved for 6 : 3 : 1-OH·C<sub>6</sub>H<sub>3</sub>Me·CHO, which with AcOH—AcO<sub>2</sub>H [(I)-free; otherwise acetylation occurs also], methylation of the product, and subsequent hydrolysis gives 3 : 1 : 4-OH·C<sub>6</sub>H<sub>3</sub>Me·OMe (III) (b) and its 4 : 1 : 3-isomeride (IV) (a); similarly 2 : 4 : 1-OH·C<sub>6</sub>H<sub>3</sub>Me·CHO yields (III) (a) and (IV) (b). *p*-OH·C<sub>6</sub>H<sub>4</sub>·CHO with Ac<sub>2</sub>O—AcO<sub>2</sub>H gives *p*-OH·C<sub>6</sub>H<sub>4</sub>·OAc and *p*-C<sub>6</sub>H<sub>4</sub>(OAc)<sub>2</sub>; with AcOH—AcO<sub>2</sub>H [(I)-free] *p*-hydroxyphenyl formate, b.p. 150°/12 mm., m.p. 57°, results. The following oxidations are also effected: *o*-OMe·C<sub>6</sub>H<sub>4</sub>·CHO to *o*-OMe·C<sub>6</sub>H<sub>4</sub>·O·CHO (99%); 3 : 4 : 1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO to 3 : 4-dimethoxyphenyl formate, m.p. 57°; *p*-OMe·C<sub>6</sub>H<sub>4</sub>·COMe to *p*-OMe·C<sub>6</sub>H<sub>4</sub>·OAc; *m*-OH·C<sub>6</sub>H<sub>4</sub>·CHO and *o*- and *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO to the corresponding acids. H. B.

**Stability of 2 : 2'-dihydroxydiphenylmethane.** C. A. Buehler, D. E. Cooper, and E. O. Scrudder (*J. Org. Chem.*, 1943, 8, 316—319).—*p*-C<sub>6</sub>H<sub>4</sub>Br·OH and CH<sub>2</sub>O in H<sub>2</sub>SO<sub>4</sub>—H<sub>2</sub>O at 80—90° give 5 : 5'-dibromo-2 : 2'-dihydroxydiphenylmethane (I), m.p. 183—184° (dibenzoate, m.p. 192°), reduced by Na in *n*-C<sub>5</sub>H<sub>11</sub>·OH at 160—170° to the stable (cf. lit.) 2 : 2'-dihydroxydiphenylmethane (II), m.p. 119—120° (dibenzoate, m.p. 76—77°), which gives xanthene when heated at 150—160° and then distilled. *o*-OH·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·OH, *p*-C<sub>6</sub>H<sub>4</sub>Cl·OH, and a little conc. HCl at 30° give 5-chloro-2 : 2'-dihydroxydiphenylmethane, m.p. 128—129° (dibenzoate, m.p. 80—81°), reduced as above to (II). With KOH—Me<sub>2</sub>SO<sub>4</sub>—COMe<sub>2</sub>—H<sub>2</sub>O, (I) gives the Me<sub>2</sub> ether, m.p. 107.5°, and thence (CrO<sub>3</sub>—AcOH) (2 : 5 : 1-OMe·C<sub>6</sub>H<sub>3</sub>Br)<sub>2</sub>CO, m.p. 123—124°. R. S. C.

**Synthetic oestrogens. II. Configuration of synthetic oestrogens.** F. von Wessely and H. Welleba (*Ber.*, 1941, 74, [B], 777—785).—A more detailed account of work previously abstracted (A., 1942, II, 89). Reduction (H<sub>2</sub>, Pd-black, AcOH) of diethylstilbestrol gives ~88% of *dl*- and 12% of *meso*-(*p*-OH·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>)<sub>2</sub>. *dl*-(CHPhMe)<sub>2</sub> has m.p. 12.5° and is obtained nearly pure by reduction of *trans*-(CPhMe)<sub>2</sub>. H. B.

**Ethers of 4-chloro-2-nitro-3 : 5-dimethylphenol.** B. Jones (*J.C.S.*, 1943, 445; cf. A., 1941, II, 221).—The *k* (0.0728) recorded for the CH<sub>2</sub>Ph ether (*loc. cit.*) is for the hexyl ether. The following are prepared: Me, m.p. 166°, Et, m.p. 107°, Pr<sup>a</sup>, m.p. 68°, *n*-C<sub>6</sub>H<sub>13</sub>, m.p. 41°, and *p*-C<sub>6</sub>H<sub>4</sub>Br·CH<sub>2</sub> ether, m.p. 105°, of 1 : 3 : 5 : 4 : 2-OH·C<sub>6</sub>HMe<sub>2</sub>Cl·NO<sub>2</sub>. The CH<sub>2</sub>Ph ether, m.p. 105°, is obtained from 4-chloro-3 : 5-dimethylphenyl CH<sub>2</sub>Ph ether, m.p. 57°, and HNO<sub>3</sub> (d 1.5)—AcOH. A. T. P.

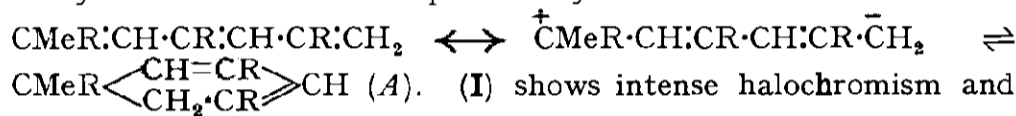
**Halogenation of phenolic ethers and anilides. XIV. *m*-Substituted phenyl ethers.** B. Jones (*J.C.S.*, 1943, 430—432; cf. A., 1941, II, 287).—Velocity coeffs. for the chlorination of *m*-C<sub>6</sub>H<sub>4</sub>X·OR (X = CO<sub>2</sub>H, R = C<sub>n</sub>H<sub>2n+1</sub> where *n* = 1—9, C<sub>12</sub>H<sub>25</sub>, [CH<sub>2</sub>]<sub>*m*</sub>·Ph where *m* = 1, 2, or 3, and *p*-C<sub>6</sub>H<sub>4</sub>Hal·CH<sub>2</sub>; X = NO<sub>2</sub>, R = Me, Et; X = Cl, R = Me, CH<sub>2</sub>Ph; X = F, R = *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>), 2 : 5 : 1-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>·OR (R = CH<sub>2</sub>Ph, *p*-C<sub>6</sub>H<sub>4</sub>Me·CH<sub>2</sub>, *p*-C<sub>6</sub>H<sub>4</sub>Br·CH<sub>2</sub>, *m*- or *p*-C<sub>6</sub>H<sub>4</sub>F·CH<sub>2</sub>), 3 : 5 : 1-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>·OR (R = Me, *p*-C<sub>6</sub>H<sub>4</sub>Br·CH<sub>2</sub>), and 5 : 2 : 1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me·OR (R = Me, Et, CH<sub>2</sub>Ph), in 99% AcOH at 20°, are given. The relative directive powers of OR groups obtained from a ratio of velocity coeffs. are very similar to those found in *p*-C<sub>6</sub>H<sub>4</sub>X·OR, where chlorination yields a single homogeneous product. The following are new: *m*-isopropoxy-, m.p. 96°, *n*-butoxy-, m.p. 62°, *n*-amyl-, m.p. 72°, *n*-hexyloxy-, m.p. 71°, *n*-heptyloxy-, m.p. 80°, *n*-octyloxy-, m.p. 73°, *n*-nonyloxy-, m.p. 84°, and *n*-dodecyloxy-, m.p. 91°, *benzyl*oxy-, m.p. 134°, *p*'-fluoro-, m.p. 148°, *chloro*-, m.p. 170°, and *bromo-benzyl*oxy-, m.p. 179°, *β*-phenylethoxy-, m.p. 110°, and *γ*-phenyl-*n*-propoxy-benzoic acid, m.p. 118°; 3 : 5-dichlorophenyl *p*-bromobenzyl ether, m.p. 68°; 4-nitro-*o*-tolyl Pr<sup>a</sup>, m.p. 51°, CH<sub>2</sub>Ph, m.p. 79°, and *p*-methylbenzyl ether, m.p. 110°; *m*-fluorophenyl *o*-nitrobenzyl ether, m.p. 53°; *m*-chlorophenyl CH<sub>2</sub>Ph ether, m.p. 65°; 2 : 5-dichlorophenyl CH<sub>2</sub>Ph, m.p. 58°, *m*-, m.p. 79°, and *p*-fluoro-, m.p. 86°, *p*-bromo-, m.p. 77°, and *p*-methyl-benzyl, m.p. 58°, ether. A. T. P.

**Applications of camphor oil. II. *cis*- and *trans*-iso-Chavibetol alkyl ethers.** E. Funakubo (*Ber.*, 1941, 74, [B], 832—840).—*trans*-isoChavibetol Me, b.p. 126°/5 mm. (prep. by aq. MeOH—NaOH—Me<sub>2</sub>SO<sub>4</sub>), Et, m.p. 49.3—50.3° (aq. EtOH—NaOH—EtI), and Pr<sup>a</sup> ether, m.p. 44.2—45.7° (EtOH—NaOH—Pr<sup>a</sup>Br at 110—130°), with Et<sub>2</sub>O—Br at room temp. give the dibromides (A), m.p. 94—95.7°, 118.5—119°, and 94—95.7° (? 97—98°), respectively, converted by KOH (<5 mols.) at >90° into 3 : 4-dimethoxy-, b.p. 139°/4 mm., 4-methoxy-3-ethoxy-, b.p. 163—164°/7 mm., and 4-methoxy-3-*n*-propoxy-Δ<sup>a</sup>-propenylbenzene, b.p. 185°/9 mm., respectively. These are reduced (1 H<sub>2</sub>, Pd-black, EtOH) to *cis*-isochavibetol Me (I), b.p. 137—137.5°/6 mm., Et, m.p. 38—39.8° (lit. 40—41°), and Pr<sup>a</sup> ether, b.p. 140—

141°/6.5 mm. (dibromide, m.p. 103—105.5°), respectively. With MeOH—KOH at room temp. (A) give 4 : 3 : 1-OMe·C<sub>6</sub>H<sub>3</sub>(OR)·CH·CMeBr [R = Et, b.p. 162—163°/3 mm., m.p. 67.3—68.8°, oxidised (aq. KOH—KMnO<sub>4</sub>) to 4 : 3 : 1-OMe·C<sub>6</sub>H<sub>3</sub>(OEt)·CO<sub>2</sub>H, m.p. 164.2—167.2° (Ag salt)]. Small amounts of KOH at higher temp. give mixtures. The *cis*-isoeugenol Me ether [= (I)] of Boedecker *et al.* (A., 1931, 348) is probably impure. Absorption spectra of the *cis*- and *trans*-ethers are given. H. B.

**Constituents of red sandalwood. III. Synthesis of pterostilbene [4-hydroxy-3' : 5'-dimethoxystilbene].** E. Späth and K. Kromp (*Ber.*, 1941, 74, [B], 189—192; cf. *ibid.*, 1940, 73, 881).—*p*-OH·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CO<sub>2</sub>H, m.p. 153—154° (lit. 150°) [obtained by demethylation (P + HI) of the OMe-acid] (as Na salt), and 3 : 5 : 1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO (I) (improved isolation) in Ac<sub>2</sub>O at 160° afford (after hydrolysis) 3 : 5-dimethoxy-*α*-*p*-hydroxyphenylcinnamic acid (II), m.p. 228—229° (vac.). The oil obtained by decarboxylation (Cu + quinoline at 240—260°) of (II), when treated with conc. aq. HCl in MeOH at 20° for 36 hr., affords (*cis* → *trans* conversion) pterostilbene, m.p. 87—88°. Similarly, Na homoanisate and (I) give 3 : 5-dimethoxy-*α*-*p*-anisylcinnamic acid, m.p. 192°, decarboxylated to an oil, converted as above into pterostilbene Me ether, m.p. 56—57°, which is identical with resveratrol Me<sub>2</sub> ether (Takaoka, A., 1940, II, 328). J. W.

**βδζ-Tri-*p*-anisyl-*α*<sup>ve</sup>-heptatriene; problem of tautomerism or mesomerism?** W. Schneider and H. Keller (*Ber.*, 1941, 74, [B], 729—755).—The compound, C<sub>28</sub>H<sub>28</sub>O<sub>3</sub> (I), m.p. 113—114°, obtained in 5—6% yield from PhOMe and SO<sub>3</sub>H·CH<sub>2</sub>·CO<sub>2</sub>H (prep. described), is considered to be βδζ-tri-*p*-anisyl-Δ<sup>ve</sup>-heptatriene; (I) may arise from CMeR·CH·CR·CH·CR·CH·COR (R = anisyl) by an acetolysis. Many of its reactions are explicable by the scheme



(I) shows intense halochromism and gives a dihydrochloride [1 HCl lost in a vac.; useful for purification of (I)], perchlorate, detonates when heated, and a dihydrobromide stannibromide, 2(I), H<sub>2</sub>SnBr<sub>6</sub>. With 75 vol.-% H<sub>2</sub>SO<sub>4</sub>, (I) (in C<sub>6</sub>H<sub>6</sub>; subsequently removed) gives first a hydrolysable halochromic salt and then a stable sulphonic acid sulphate, C<sub>28</sub>H<sub>27</sub>O<sub>3</sub>·SO<sub>3</sub>H·H<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O, green, m.p. 120—125°; with H<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O at 70° a trisulphonic acid [amorphous Ba salt, (C<sub>28</sub>H<sub>25</sub>O<sub>12</sub>S<sub>3</sub>)<sub>2</sub>Ba<sub>3</sub>] results. (I) absorbs 2 H<sub>2</sub> on reduction (Pd—BaSO<sub>4</sub>, AcOH) but titration with *o*-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (II) shows 3 double linkages. Demethylation (aq. AcOH—HBr) of (I) gives 3 : 5-di-*p*-hydroxyphenyltoluene (+2H<sub>2</sub>O), m.p. 100° (loss of H<sub>2</sub>O; rapid heating), 108° (slow) resolidifying with m.p. 140° (diacetate, m.p. 139°), presumably formed by loss of PhOH from the intermediate (A, R = *p*-OH·C<sub>6</sub>H<sub>4</sub>). (CH·CO)<sub>2</sub>O and (I) in boiling C<sub>6</sub>H<sub>6</sub> give (mainly) amorphous material and ~20% of an adduct, C<sub>32</sub>H<sub>30</sub>O<sub>6</sub>, m.p. 201—202°, which could not be reduced but contains one C·C [titration with (II)]. (I) is dehydrogenated by AcOH—Br or -30% H<sub>2</sub>O<sub>2</sub> to a compound, C<sub>28</sub>H<sub>26</sub>O<sub>3</sub> (III), m.p. 133—134°. Whilst oxidative degradation of (I) is inconclusive, (III) with AcOH—CrO<sub>3</sub> gives anisic acid and ~50% of anisil, thus indicating that it is 2 : 3 : 5-tri-*p*-anisyltoluene, formation of which involves migration of anisyl. Reduction (H<sub>2</sub>, PtO<sub>2</sub>, AcOH) of (I) results in absorption of 12—13 H<sub>2</sub> and gives a mixture. *s*-Tri-*p*-anisylbenzene similarly affords a mixture containing ~5% of 1 : 3 : 5-tricyclohexylcyclohexane, m.p. 157—159°, also obtained (<5%) from *s*-C<sub>6</sub>H<sub>3</sub>Ph<sub>3</sub>; the behaviour of related compounds [e.g., PhOMe, CH(C<sub>6</sub>H<sub>4</sub>·OMe)<sub>3</sub>] is investigated. H. B.

***N*-Nitroalkyl-*p*-aminophenols.**—See B., 1943, II, 340.

**Kerr effect in solutions of *p*-azoxyanisole.**—See A., 1943, I, 298.

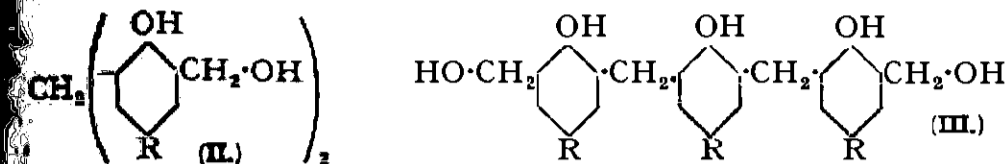
**4-Nitro- and 4-amino-4'-acylamidodiphenyl sulphones.**—See B., 1943, III, 279.

**4 : 2' : 5'-Triaminodiphenyl sulphone and derivatives.**—See B., 1943, III, 279.

**Ultra-violet absorption of formaldehyde-phenol resins.**—See A., 1943, I, 295.

**Hardening process of phenol-formaldehyde resins. IV. A.** Zinke and F. Hanus [with H. Prenschütz-Schützenau, H. Troger, and (in part) R. Möldner and K. Lercher] (*Ber.*, 1941, 74, [B], 205—214; cf. A., 1939, II, 476).—The course of the hardening of 1 : 4 : 2 : 6- (I) and 1 : 2 : 4 : 6-OH·C<sub>6</sub>H<sub>2</sub>R(CH<sub>2</sub>·OH)<sub>2</sub> is bound up with the step-wise elimination of H<sub>2</sub>O and CH<sub>2</sub>O; when R is a large substituent the two processes can be separated. Firstly, loss of H<sub>2</sub>O leads to ether linkings since HBr affords bromides corresponding to the starting materials. In hardening, small amounts of cryst. sublimates are formed consisting of OH·C<sub>6</sub>H<sub>2</sub>R(CHO)<sub>2</sub>; their formation is attributed to "cracking" and disproportionation of the -CH<sub>2</sub>·O·CH<sub>2</sub>- linkings and analogous cases are already known. The elimination of CH<sub>2</sub>O is less easy to interpret. Assuming that a macromol. with CH<sub>2</sub> linkings between nuclei is formed, 1 mol. of CH<sub>2</sub>O should arise from 1 mol. of dicarbinol but the max. found is 0.6 mol. The deficit must participate in further reactions such as formation of CH<sub>2</sub>: ethers with phenolic OH groups, or CH<sub>2</sub> bridges

with reactive nuclear positions forming cross linkings in the macromols. These processes should result in  $\text{H}_2\text{O}$ -formation in excess of 1 mol. which is, in fact, observed. Some  $\text{CH}_2\text{O}$  is used in methylating OH groups since the resins from (I) ( $\text{R} = \text{Me}$  and  $\text{Cl}$ ) contain respectively 0.5 and 1.6% OMe. The *p*-toluenesulphonates of the phenol-dicarbonyls with esterified phenolic OH give no  $\text{CH}_2\text{O}$  and the products contain ether linkings. It is suggested that  $\text{CH}_2\text{O}$  may condense with the  $\text{CH}_2$  groups linking benzene nuclei and confirmation is



sought, and found, in the behaviour of (II) ( $\text{R} = \text{Me}$  or  $\text{Cl}$ ), (III) ( $\text{R} = \text{Me}$  or  $\text{Cl}$ ), and (IV) ( $\text{R} = \text{Me}$  or  $\text{Cl}$ ) which contain preformed  $\text{CH}_2$  groups; these substances give less  $\text{CH}_2\text{O}$  and much more  $\text{H}_2\text{O}$  in proportion than do the mononuclear dicarbonyls. 4:4'-Dihydroxy-3:5:3':5'-tetra(hydroxymethyl)diphenylmethane (V) affords 2 mols. of  $\text{H}_2\text{O}$  and only a trace of  $\text{CH}_2\text{O}$ . (III) ( $\text{R} = \text{Cl}$ ) affords a *pentaacetate*, m.p.  $142^\circ$ , and the *tetrabromide*, from (V) has m.p. (crude)  $169^\circ$ . J. W. A.

**Hardening processes of phenol-formaldehyde resins. VI.** "Salireton" [di-*o*-hydroxybenzyl ether]. E. Ziegler (*Ber.*, 1941, 74, [B], 841—844).— $\text{o-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$  at  $140^\circ$  alone or in glycerol gives ~10 or ~16% respectively of ( $\text{o-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ )<sub>2</sub>O, m.p.  $122$ — $123^\circ$  (*dibenzoate*, m.p.  $115^\circ$ ) (cf. Giacosa, A., 1880, 716), which when heated above its m.p. affords  $\text{o-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  (I). 2:3:5:1-OH·C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>·CH<sub>2</sub>·OH and -OH·C<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>·CH<sub>2</sub>·OH with PhCHO in aq. EtOH-HCl give the 1:2-CHPh: ethers, m.p.  $46^\circ$  and  $87$ — $88^\circ$ , respectively. 4:4'-Dihydroxy-3:3'-dimethyl-5:5'-di(hydroxymethyl)diphenylmethane similarly affords the 4:5:4':5'-(CHPh)<sub>2</sub> ether, m.p.  $140^\circ$ ; (I) gives no cryst. product. H. B.

**Hardening processes of phenol-formaldehyde resins. V.** A. Zinke and E. Ziegler (*Ber.*, 1941, 74, [B], 541—545).—2:3:5:1-OH·C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>·CH<sub>2</sub>·OH (I) at  $135$ — $140^\circ$  (bath)/1 hr. gives 2:2'-dihydroxy-3:5:3':5'-tetramethyldibenzyl ether, m.p.  $100$ — $101^\circ$ , converted [as is (I)] by HCl-C<sub>6</sub>H<sub>6</sub> into 2:3:5:1-OH·C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>·CH<sub>2</sub>Cl, m.p.  $59^\circ$ , and by boiling 3% NaOH into 2:2'-dihydroxy-3:5:3':5'-tetramethyldiphenylmethane, m.p.  $148^\circ$  [also obtained when 2:3:5:1-ONa·C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>·CH<sub>2</sub>·OH is fused or heated at  $130$ — $140^\circ$ /vac., whereby  $\text{CH}_2\text{O}$  is evolved]. 4-Hydroxy-3-methoxy-5-hydroxymethylallylbenzene [eugenol alcohol] (II) resinifies when heated, but the 4-ONa derivative at  $200^\circ$  or, better,  $125^\circ$ /vac. gives 2:2'-dihydroxy-3:3'-dimethoxy-5:5'-diallyldiphenylmethane, m.p.  $84^\circ$ , also obtained from (II) and an excess of boiling 5% NaOH or from eugenol,  $\text{CH}_2\text{O}$ , and KOH. Reactions of OH-alcohols of type (I) are thus influenced by alkali. H. B.

**Symmetrical diaryldialkylethanediols. I.**  $\beta\gamma$ -Diphenylbutane- $\beta\gamma$ -diol. E. J. H. Chu and J. C. Chu (*J. Chinese Chem. Soc.*, 1942, 9, 190—195).—Both modifications of (CPhMe·OH)<sub>2</sub> with AcOH-I yield CPhMe<sub>2</sub>·COPh. F. R. G.

**Catalytic hydrogenation of dimedone (dimethyldihydroresorcinol), and a preparation of 1:1-dimethylcyclopentane.** T. Henshall (*J.S.C.I.*, 1943, 62, 127—128).—Dimedone has been hydrogenated under pressure in the presence of the Raney Ni catalyst, to furnish 3:3-dimethylcyclohexanol (I) (75% yield) and 3:3-dimethylcyclohexane-1:5-diol. (I) has been converted into 1:1-dimethylcyclopentane.

**Mechanism of formation of leuco-triphenylmethane dyes, and an analogy in the Perkin reaction.** R. R. Davies and H. H. Hodgson (*J. Soc. Dyers and Col.*, 1943, 59, 196—198).—The mechanism of the formation of leuco-triphenylmethane dyes appears to be a two-stage process, viz., (a) an initial aldol condensation between ArCHO and 1 mol. of arylamine, and (b) elimination of  $\text{H}_2\text{O}$  between the aldol and a second mol. of amine. Condensation of  $\text{o-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  (I) (1 mol.) (prep. from  $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$  and aq.  $\text{Na}_2\text{SO}_3$  at  $170$ — $175^\circ$ /130—140 lb. per sq. in.) and NPhEt<sub>2</sub> (2 mols.) at  $105$ — $110^\circ$  is examined in detail. Whereas only 2% of (I) is uncondensed after 18 hr., optimum production of the leuco-compound is obtained only after 36 hr.; the aldol stage seems to be attained quickly. The leuco-compound is oxidised by  $\text{PbO}_2$ -aq. AcOH and the dye estimated by  $\text{TiCl}_2$ . The mechanism of reaction is discussed. In standard Perkin reactions of PhCHO,  $\text{o-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , or  $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$  with NaOAc-Ac<sub>2</sub>O at  $\sim 180^\circ$ , yields of CHPh:CH·CO<sub>2</sub>H, coumarin, and  $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$  are 68, 43, and 47%, respectively, thus showing the electron-repelling effect of the OH and of the mesomeric Cl in decreasing the amount of aldol formation. A. T. P.

**Absorption of light by organic molecules and ions according to quantum mechanics.**—See A., 1943, I, 295.

**Acidity constants, resonance energies, and light absorption of simple dyes.**—See A., 1943, I, 296.

**Effect of acidifying substituents on chromophoric systems.**—See A., 1943, I, 296.

**Preparation of substituted phenylacetic acids.** C. Schöpf and L. Winterhalder [with W. Salzer] (*Annalen*, 1940, 544, 62—77).—Methods of preparing these acids are discussed and some are investigated. 3:4:1-CH<sub>2</sub>Ph·O·C<sub>6</sub>H<sub>3</sub>(OMe)·CHO (modified prep.), m.p.  $62^\circ$ , with  $\text{H}_2$ -PtO<sub>2</sub>-MeOH or Al(OPr<sup>i</sup>)<sub>3</sub>-Pr<sup>i</sup>OH at  $95^\circ$  (removal of COMe<sub>2</sub> as formed) gives good yields of 3-benzyloxy-4-methoxybenzyl alcohol (I), m.p.  $73^\circ$ , which with  $\text{SOCl}_2$ -C<sub>5</sub>H<sub>5</sub>N-CHCl<sub>3</sub> at  $-5^\circ$  to  $0^\circ$  gives the *chloride* (II), m.p.  $79^\circ$ . With NaCN in MeOH, (II) gives 3-benzyloxy-4-methoxybenzyl Me ether, m.p.  $58^\circ$ , but in boiling EtOH-H<sub>2</sub>O (not C<sub>6</sub>H<sub>6</sub>-H<sub>2</sub>O) gives about equal parts of the oily nitrile and Et ether (III) with probably some (I). With boiling KOH-EtOH-H<sub>2</sub>O, this mixture gives 3:4:1-CH<sub>2</sub>Ph·O·C<sub>6</sub>H<sub>3</sub>(OMe)·CH<sub>2</sub>·CO<sub>2</sub>H (IV); the unchanged (III) with Et<sub>2</sub>O-HCl affords (II). HNO<sub>3</sub> (*d* 1.4) in AcOH converts (IV) into the 6-NO<sub>2</sub>-acid, sinters  $158^\circ$ , m.p.  $178$ — $179^\circ$ , hydrolysed to 3:4:6:1-OH·C<sub>6</sub>H<sub>2</sub>(OMe)(NO<sub>2</sub>)·CH<sub>2</sub>·CO<sub>2</sub>H, m.p.  $192^\circ$  (Me ether, m.p.  $203^\circ$ ) (A., 1927, 365). Me gallate (prep. by HCl-MeOH), m.p.  $198^\circ$ , Me<sub>2</sub>SO<sub>4</sub>, and NaOH in aq. MeOH at  $35$ — $40^\circ$  and then the b.p. gives much 4-Me ether, m.p.  $136^\circ$  (lit.  $143$ — $147^\circ$ ), which with CH<sub>2</sub>PhCl and K<sub>2</sub>CO<sub>3</sub> in boiling MeOH (later also C<sub>6</sub>H<sub>6</sub>) gives Me gallate 4-Me 3:5-(CH<sub>2</sub>Ph)<sub>2</sub> ether (V) (52%), m.p.  $121$ — $122^\circ$ , and a residue converted by boiling KOH-EtOH-H<sub>2</sub>O into 2:6-dibenzyloxy-anisole, m.p.  $106^\circ$ , and gallic acid (CH<sub>2</sub>Ph)<sub>3</sub> ether, m.p.  $187^\circ$ . The acid, m.p.  $173^\circ$ , obtained from (V) by KOH-EtOH-H<sub>2</sub>O, with SOCl<sub>2</sub> at  $50$ — $60^\circ$  gives the *chloride*, m.p.  $125^\circ$ , and thence  $\omega$ -diazo-3:5-dibenzyloxy-4-methoxyacetophenone, m.p.  $92^\circ$ , which with a little conc. HCl in EtOH gives 3:5-dibenzyloxy-4-methoxyphenacyl chloride, m.p.  $93^\circ$ , and with Ag<sub>2</sub>O in MeOH at  $50^\circ$ , followed by boiling KOH-EtOH-H<sub>2</sub>O, yields 3:5-dibenzyloxy-4-methoxyphenylacetic acid (70%), m.p.  $138$ — $139^\circ$ . R. S. C.

**Transamination reaction. Mechanism of the reaction between  $\alpha$ -keto-acids and  $\alpha$ -NH<sub>2</sub>-acids.** R. M. Herbst and D. Rittenberg (*J. Org. Chem.*, 1943, 8, 380—389).—The  $\alpha$ -H of the NH<sub>2</sub>-acid is not involved in uncatalysed *in vitro* transamination. Firstly, when NH<sub>2</sub>·CHPh·CO<sub>2</sub>H (I) and AcCO<sub>2</sub>H are boiled in H<sub>2</sub>O containing 3.5% of D<sub>2</sub>O, the PhCHO produced has > a trace of D. The NH<sub>2</sub>·CHMe·CO<sub>2</sub>H (II) produced has ~2 D, of which only a small part is on C<sub>(a)</sub>; most of the D enters the Me by a secondary reaction, for oxidation of (II) by Ag<sub>2</sub>O-D<sub>2</sub>O gives AcOH containing D in the Me and shaking AgOAc with D<sub>2</sub>O introduces D; during transamination a labile intermediate,  $>\text{CH}\cdot\text{NH}\cdot\text{C}(\text{CH}_3)\cdot\text{CO}_2\text{H} \rightleftharpoons >\text{CH}\cdot\text{N}:\text{CMe}\cdot\text{CO}_2\text{H}$ , may be involved. Secondly, NH<sub>2</sub>·CDPh·CO<sub>2</sub>H (III) with AcCO<sub>2</sub>H in H<sub>2</sub>O gives (II) free from D and PhCDO ( $\rightarrow$  CHDPh·OH + BzOH free from D). (III) is prepared by shaking (I) in D<sub>2</sub>O, the exchange being slightly catalysed by H<sup>+</sup> and much by OH<sup>-</sup>. Only a small part of the  $\alpha$ -D is removed from (II) when it is converted into the 3-phenyl-5-methylhydantoin and treated with alkali. Transamination proceeds by the reactions:  $\text{NH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H} + \text{COR}'\cdot\text{CO}_2\text{H} \rightarrow \text{CO}_2\text{H}\cdot\text{CHR}\cdot\text{N}:\text{CR}'\cdot\text{CO}_2\text{H} \rightarrow \text{H}^+ + \text{CO}_2 + \text{CHR}:\text{N}\cdot\text{C}\cdot\text{R}'\cdot\text{CO}_2\text{H} \rightarrow (+\text{H}^+) \text{CHR}:\text{N}\cdot\text{CHR}'\cdot\text{CO}_2\text{H} \rightarrow (+\text{H}_2\text{O}) \text{RCHO} + \text{NH}_2\cdot\text{CHR}'\cdot\text{CO}_2\text{H}$ . R. S. C.

**Syntheses in the phenanthrene series.** G. Blumenfeld (*Ber.*, 1941, 74, [B], 524—531).—CHPh:CH·CH:CH<sub>2</sub> (I) (prep. in 39% yield from MgPhBr and CHMe:CH·CHO) with CH<sub>2</sub>:CH·CHO in boiling C<sub>6</sub>H<sub>6</sub>-quinol give 2-phenyl- $\Delta^3$ -tetrahydrobenzaldehyde (69%) (II), b.p.  $150^\circ$ /12 mm., which with CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> in C<sub>5</sub>H<sub>5</sub>N-piperidine affords 2-phenyl- $\Delta^3$ -tetrahydrocinnamic acid, m.p.  $107^\circ$  [Et ester, b.p.  $192^\circ$ /13 mm. (III), obtained with an isomeride, b.p.  $182^\circ$ /13 mm., from (II), EtOAc, and Na; both forms are hydrolysed (EtOH-KOH) to the acid; *hydrazide*, m.p.  $180^\circ$ , from (III) only]. Reduction (H<sub>2</sub>, Raney Ni, EtOH) of (II) gives 2-phenylhexahydrobenzyl alcohol (IV), ? b.p.  $162$ — $166^\circ$ /13 mm. (*dinitrobenzoate*, m.p.  $101^\circ$ ); Al(OPr<sup>i</sup>)<sub>3</sub>-C<sub>6</sub>H<sub>6</sub> affords 2-phenyl- $\Delta^3$ -tetrahydrobenzyl alcohol, b.p.  $163^\circ$ /12 mm. The *chloride*, b.p.  $148^\circ$ /12 mm., from (IV) and PCl<sub>5</sub>-CHCl<sub>3</sub> is converted (Grignard) into 2-phenylhexahydrophenylacetic acid, m.p.  $112^\circ$ , cyclised by warm conc. H<sub>2</sub>SO<sub>4</sub> to *trans*-9-keto-1:2:3:4:9:10:11:12-octahydrophenanthrene, m.p.  $96^\circ$ . CH<sub>2</sub>:CH·CO<sub>2</sub>H and (I) in boiling PhMe-quinol give 2-phenyl- $\Delta^3$ -tetrahydrobenzoic acid (V), m.p.  $122^\circ$ . The Me ester, b.p.  $162^\circ$ /14 mm., of (V) is hydrogenated (Raney Ni, MeOH) and then hydrolysed to the -hexahydrobenzoic acid, which is converted (warm conc. H<sub>2</sub>SO<sub>4</sub> or *chloride* with AlCl<sub>3</sub>-CS<sub>2</sub>) into hexahydrofluorenone (*semicarbazone*, m.p.  $204^\circ$ ). CH<sub>2</sub>:CH·CO<sub>2</sub>Et and (I) at  $100^\circ$  give the Et ester (VI), b.p.  $155$ — $160^\circ$ /15 mm., of a stereoisomeride (m.p.  $103^\circ$ ) [also obtained by oxidation of (II)] of (V) (cf. Lehmann *et al.*, A., 1935, 978). Hydrogenation of (VI) and subsequent hydrolysis (aq. EtOH-KOH) affords 2-phenylhexahydrobenzoic acid, m.p.  $110^\circ$ . H. B.

**Benzoylation of erythritol and preparation of derivatives of O-benzoylglycollaldehyde.**—See A., 1943, II, 350.

**3:4-Dinitro-benzonitrile and -benzaldehyde.** H. Goldstein and R. Voegeli (*Helv. Chim. Acta*, 1943, 26, 1125—1128; cf. A., 1943, II, 192).—NO<sub>2</sub> at C<sub>(4)</sub> is mobile in the compounds 1:3:4-C<sub>6</sub>H<sub>3</sub>R(NO<sub>2</sub>)<sub>2</sub> in which R = CO<sub>2</sub>H, CN, or CHO. 3:4-Dinitrobenzonitrile (I), m.p.  $92^\circ$  (corr.), is not satisfactorily obtained by Sand-

meyer's reaction from 3 : 4 : 1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·NH<sub>2</sub> but is prepared in 91% yield from 3 : 4 : 1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO·NH<sub>2</sub> and boiling SOCl<sub>2</sub>. It is hydrolysed by H<sub>2</sub>SO<sub>4</sub>-AcOH-H<sub>2</sub>O to 3 : 4 : 1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>H and converted by hot dil. NaOH into 4 : 3 : 1-OH·C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>·CO<sub>2</sub>H. (I) is converted by NH<sub>3</sub>-EtOH, NH<sub>2</sub>Ph·K<sub>2</sub>CO<sub>3</sub>, and piperidine into 3 : 4 : 1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)<sub>2</sub>·CN, 3 : 4 : 1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(NHPh)·CN and 3-nitro-4-piperidinobenzonitrile, respectively. 1 : 3 : 4-C<sub>6</sub>H<sub>3</sub>Me(NO<sub>2</sub>)<sub>2</sub> is transformed by CrO<sub>3</sub> in Ac<sub>2</sub>O-conc. H<sub>2</sub>SO<sub>4</sub> into 3 : 4-dinitrobenzylidene diacetate, m.p. 94—95° (corr.), hydrolysed by boiling HCl to 3 : 4 : 1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO, m.p. 64° (corr.). This yields NaNO<sub>2</sub> when treated with boiling dil. NaOH. The action of NH<sub>2</sub>Ph or NHPh·NH<sub>2</sub> in presence of K<sub>2</sub>CO<sub>3</sub> establishes the mobility of NO<sub>2</sub> (probably but not definitely) at C<sub>4</sub>. H. W.

**Chlorine substitution products of veratraldehyde, veratric acid, and related compounds.** L. C. Raiford and D. E. Floyd (*J. Org. Chem.*, 1943, 8, 358—366).—Vanillin and Cl<sub>2</sub> in CHCl<sub>3</sub> at 40—50° give 4 : 5 : 3 : 1-OH·C<sub>6</sub>H<sub>3</sub>Cl(OMe)·CHO, converted in aq. NaHCO<sub>3</sub> by Me<sub>2</sub>SO<sub>4</sub> at ~70° into 3 : 4 : 5 : 1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Cl·CHO; with fuming HNO<sub>3</sub> at 0—10° this gives 5-chloro-6-nitroveratraldehyde, m.p. 122—123°, oxidised by KMnO<sub>4</sub> in aq. C<sub>6</sub>H<sub>5</sub>N at 50—60° to 5-chloro-6-nitro-, m.p. 190—191°, which yields 5-chloro-6-amino-, m.p. 188—189°, and thence 5 : 6-dichloro-veratric acid, m.p. 186—187° (Me ester, m.p. 95—96°) (cf. Mazzara, A., 1901, i, 720). 3 : 4 : 1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO gives similarly 3 : 4 : 6 : 1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Cl·CHO, and thence 6-chloro-2-nitro-veratraldehyde (I), m.p. 101—102°, and -veratric acid, m.p. 192—193°, and 6-chloro-2-aminoveratric acid (II), m.p. 163—165°. 3 : 4 : 1-OMe·C<sub>6</sub>H<sub>3</sub>(OAc)·CH(OAc)<sub>2</sub> gives the 6-Cl-derivative and thence, by way of its acetate, 2 : 6 : 3 : 4 : 1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Cl(OMe)(OH)·CHO, which yields (I) and, successively, 2 : 6 : 3 : 4 : 1-NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Cl(OMe)(OH)·CHO, 3 : 2 : 6 : 4 : 1-OMe·C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>(OH)·CHO, 2 : 6-dichloro-veratraldehyde, m.p. 119—120°, and -veratric acid, m.p. 115° [also obtained from (II)]. Similar reactions lead to 6-bromo-2-amino-, m.p. 101°, 2 : 6-dibromo-, m.p. 137°, 5-chloro-2-, m.p. 62—63°, 6-chloro-5-, m.p. 127—128°, 2-chloro-5-, m.p. 51—52°, and 5-chloro-6-bromo-, m.p. 119—120°, 2 : 5 : 6-tribromo-, m.p. 129—130°, 5-chloro-2-nitro-, m.p. 51—52°, 2 : 5 : 6-trichloro-, m.p. 55°, 2 : 5 : 6-trichloro-, m.p. 94—95°, and 5-iodo-, m.p. 72—73°, -veratraldehyde and 2-, m.p. 200—202°, 5-, m.p. 189—190°, and 6-chloro-, m.p. 175—176°, 2 : 5-dichloro-, m.p. 164—165° (Me ester, b.p. 185—187°/5 mm.), 2 : 5 : 6-trichloro-, m.p. 123—124°, and -tribromo-, m.p. 169—170°, 5-chloro-2-, m.p. 175—176°, 2-chloro-5-, m.p. 183—184°, 6-chloro-5-, m.p. 189—190°, and 5-chloro-6-bromo-, m.p. 178—179°, 5-chloro-2-nitro-, m.p. 179—180°, 6-bromo-2-nitro-, m.p. 198—199°, 6-bromo-2-amino-, m.p. 182°, and 5-iodo-veratric acid, m.p. 184—185°. R. S. C.

**Volatile plant substances. XXIV. Composition of the essential oil and resin of lovage (*Levisticum officinale*, Koch).** Y. R. Naves (*Helv. Chim. Acta*, 1943, 26, 1281—1295).—o-CHO·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H with MgBu<sup>+</sup>Br affords α-n-butylphthalide (I), b.p. 141°/2.4 mm. o-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O, n-valeric anhydride, and Na n-valerate give n-butylidenephthalide, b.p. 141°/2.4 mm., hydrogenated (Raney Ni in 95% EtOH) to (I) and (PtO<sub>2</sub> in AcOH) to α-n-butylhexahydrophthalide, b.p. 129°/1.3 mm., which is hydrolysed (50% KOH) to o-α-hydroxyamylhexahydrobenzoic acid, m.p. 97—97.5° (benzylthiuronium salt, m.p. 131.5—132°). H. W.

**Identification of aromatic carboxylic acids as ureides. II.** F. Zetsche and G. Voigt (*Ber.*, 1941, 74, [B], 183—188; cf. A., 1940, II, 129).—N-Aroyl-NN'-di-p-dimethylaminophenylcarbamides are prepared from ArCO<sub>2</sub>H and (p-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N)<sub>2</sub>C in a solvent (Et<sub>2</sub>O, EtOH, C<sub>6</sub>H<sub>6</sub>, or COMe<sub>2</sub>) and the colours of the products recorded in terms of W. Ostwald's colour nomenclature. o-Substituents, except NO<sub>2</sub>, exert a hypsochromic effect. The o-, m.p. 152—153°, m-, m.p. 240°, and p-amino-, sinters from ~250°, o-, m.p. 166°, m-, m.p. 137°, and p-salicylideneamino-, m.p. 207°, o-, m.p. 169—170°, m-, m.p. 115°, and p-benzoyl-, m.p. 154°, o-, m.p. 161°, m-, m.p. 138.5°, and p-nitro-, m.p. 210°, 2-methoxy-3-, m.p. 151°, -4-, m.p. 122°, and -5-methyl-, m.p. 153°, p-dimethylamino-, m.p. 205—212° (sinters and darkens from 157°), o-anilino-, m.p. 145°, o-phenyl-, m.p. 140°, and 4-nitro-2-amino-, m.p. 176° (darkens 170—172°), -benzoyl-, o-, m.p. 162°, m-, m.p. 170°, and p-nitrocinnamoyl-, m.p. 178° (sinters 175°), and 2 : 6-dimethylpyridoyl-, m.p. 151°, -derivatives are described. J. WA.

**Lichen substances. XCVI. New depside "hypothamnolic acid."** Y. Asahina, M. Aoki, and F. Fuzikawa (*Ber.*, 1941, 74, [B], 824—831).—Et<sub>2</sub>O extraction of (so-called) *Cladonia uncialis* (f. *obtusata*) (Japanese) yields usnic and hypothamnolic acid (I), C<sub>19</sub>H<sub>18</sub>O<sub>10</sub>, m.p. 217—218° (decomp.), but no squamatic acid (cf. A., 1933, 159). CH<sub>2</sub>N<sub>2</sub> then gives the Me<sub>2</sub> ester (II), m.p. 197—198°, or Me<sub>2</sub> ester Me<sub>3</sub> ether, m.p. 127°, which are cleaved by cold conc. H<sub>2</sub>SO<sub>4</sub> to 3-Me 1-H 2-hydroxy-4-methoxy-6-methylisophthalate (III) and Me 2 : 4 : 5-trihydroxy-3 : 6-dimethylbenzoate (IV), m.p. 151—152°, or 3-Me 1-H 2 : 4-dimethoxy-6-methylisophthalate and Me 5-hydroxy-2 : 4-dimethoxy-3 : 6-dimethylbenzoate, m.p. 45°, respectively. Reduction (2 H<sub>2</sub>, Pd-C, AcOH) of the Me<sub>2</sub> ester, m.p. 158°, of thamnolic acid, m.p. 222°, gives (II). 1 : 4 : 2 : 3 : 5-C<sub>6</sub>HMe<sub>2</sub>(OH)<sub>3</sub>, Zn(CN)<sub>2</sub>, and Et<sub>2</sub>O-HCl afford 2 : 4 : 5-trihydroxy-3 : 6-dimethylbenzaldehyde,

m.p. 193°, the triacetate, m.p. 148° (prep. by Ac<sub>2</sub>O-C<sub>6</sub>H<sub>5</sub>N), of which is oxidised (aq. KMnO<sub>4</sub>-COMe<sub>2</sub>-MgSO<sub>4</sub> at 45°) to 2 : 4 : 5-triacetoxy-3 : 6-dimethylbenzoic acid, m.p. 142—143° (Me ester, m.p. 197—198°), hydrolysed to the (OH)<sub>3</sub>-acid, m.p. 190° [Me ester = (IV)]. (III) and ClCO<sub>2</sub>Et in COMe<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>N give a mixed anhydride, C<sub>17</sub>H<sub>20</sub>O<sub>10</sub>, m.p. 81°, hydrolysed (aq. COMe<sub>2</sub>-NaHCO<sub>3</sub>) to 3-Me 1-H 4-methoxy-2-carbomethoxy-6-methylisophthalate, m.p. 127.5° (cf. A., 1937, II, 102), the chloride (SOCl<sub>2</sub>) from which with (IV) affords Me<sub>2</sub> carbomethoxyhypothamnolate, m.p. 178°, and thence (II). (I) has the structure shown. H. B.

**5-Amino-2-sulphanilylbenzoic acid and derivatives.**—See B., 1943, II, 341.

**Derivatives of 3 : 4-dihydroxy-2-carboxyphenylacetic acid.** C. Schöpf, I. Jäckh-Tettweiler, G. Mayer, H. Perrey-Fehrenbach, and L. Winterhalder (*Annalen*, 1940, 544, 77—100).—Meconinecarboxylic acid (prep. from opianic acid by aq. NaCN at ~5—8° and then conc. HCl at 100°; 80% yield) with boiling HBr and then red P-HI (d 1.7) at 135° gives 3 : 4-dihydroxy-2-carboxyphenylacetic acid (I) (~50—60%), m.p. 220° (yellow at 212°) (blue FeCl<sub>3</sub> colour), and with aq. KMnO<sub>4</sub> yields 2-carboxy-3 : 4-dimethoxyphenylglyoxylic acid, m.p. 98°, which undergoes ring-closure when reduced. Evaporating meconinylacetic acid (II) with 50% aq. KOH gives 2-carboxy-3 : 4-dimethoxycinnamic acid (80%), m.p. 178—180° [with warm acid regenerates (II)], hydrogenated (Pd-CaCO<sub>3</sub>) as Na<sub>2</sub> salt in H<sub>2</sub>O to β-2-carboxy-3 : 4-dimethoxyphenylpropionic acid, +2H<sub>2</sub>O, m.p. 125—127°, which with Ac<sub>2</sub>O at the b.p. and then 200° yields CO<sub>2</sub> and 6 : 7-dimethoxy-α-hydrindone (64%), m.p. 40—43° [semicarbazone, +H<sub>2</sub>O and anhyd., sinters 214°, m.p. 217—219° (decomp.)]. The derived (amyl nitrite-conc. HCl-MeOH at 0° and then 50°) 2-OH·N<sup>+</sup> derivative, m.p. 209—211°, with PCl<sub>5</sub>-Et<sub>2</sub>O gives 2-carboxy-3 : 4-dimethoxybenzyl cyanide, m.p. 104—108°, with, sometimes, 2-carboxy-3 : 4-dimethoxyphenylacetamide, m.p. 176—178°, hydrolysed by aq. KOH to 2-carboxy-3 : 4-dimethoxyphenylacetic acid (III), m.p. 115—117° (lit. an oil), which is also obtained from (I) by Me<sub>2</sub>SO<sub>4</sub>-NaOH (40° and then, for hydrolysis, the b.p.) and with 57% HI-AcOH gives 3-hydroxy-2-carboxy-4-methoxyphenylacetic acid (IV), sinters 190°, m.p. 209—210° (decomp.) (bluish-violet FeCl<sub>3</sub> colour; 3-Et ether, m.p. 135—140°). Boiling MeOH-H<sub>2</sub>SO<sub>4</sub> converts (I) into the Me<sub>2</sub> ester (V), m.p. 135—136° (and some Me 3 : 4-dihydroxy-2-carboxyphenylacetate, m.p. 196—198°, which can be further esterified), which with CH<sub>2</sub>PhCl-K<sub>2</sub>CO<sub>3</sub>-MeOH gives 2 : 3 : 4 : 1-CO<sub>2</sub>Me·C<sub>6</sub>H<sub>2</sub>(O·CH<sub>2</sub>Ph)<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Me (VI), an oil, hydrolysed successively to 2-carbomethoxy-, m.p. 100—102°, and 2-carboxy-3 : 4-dibenzoyloxyphenylacetic acid, m.p. 160—166°. Similar treatment of (IV) gives Me 3-hydroxy-2-carbomethoxy-4-methoxyphenylacetate, m.p. 96—101° [bluish-violet FeCl<sub>3</sub> reaction; the impure derived 2-CO<sub>2</sub>H-ester has m.p. 103—112°; 3-CH<sub>2</sub>Ph ether (VII), m.p. 60—65°], 2-carboxy- (VIII), m.p. 128—131°, and 2-carbomethoxy-3-benzoyloxy-4-methoxyphenylacetic acid, m.p. 85—87°. With CH<sub>2</sub>N<sub>2</sub>-Et<sub>2</sub>O, (III) gives the Me<sub>2</sub> ester, b.p. 203—205°/15 mm., and thence by half hydrolysis 2-carbomethoxy-3 : 4-dimethoxyphenylacetic acid, sinters 75°, m.p. 83—85°; short treatment of (III) with HCl-MeOH gives Me 2-carboxy-3 : 4-dimethoxyphenylacetate, m.p. 110—112°. With 1 mol. of CH<sub>2</sub>PhCl and K<sub>2</sub>CO<sub>3</sub> in MeOH, (V) gives (VI), unchanged (V), and a mixture, rapidly hydrolysed by aq. NaOH at room temp. to 3-hydroxy-2-carbomethoxy-4-, m.p. 179—184° (blue FeCl<sub>3</sub> colour), and 4-hydroxy-2-carbomethoxy-3-benzoyloxyphenylacetic acid, m.p. 112—116° (no FeCl<sub>3</sub> colour), converted by prolonged hydrolysis at 100° into 3-hydroxy-2-carboxy-4- (IX), m.p. 186—188°, and 4-hydroxy-2-carboxy-3-benzoyloxyphenylacetic acid, m.p. 160—163°, respectively, and by CH<sub>2</sub>N<sub>2</sub> into Me 2-carbomethoxy-4-benzoyloxy-3-methoxyphenylacetate, an oil (and a substance, m.p. 138—143°), and (VII), respectively, which by prolonged hydrolysis give 2-carboxy-3-benzoyloxy-3-methoxyphenylacetic acid, m.p. 177—179°, and (VIII), respectively. With CH<sub>2</sub>PhCl (1 mol.) and NaOMe-MeOH, (V) gives Me 3-hydroxy-2-carbomethoxy-4-benzoyloxyphenylacetate, m.p. 90—95°, and thence (IX). Opianic acid Me ψ-ester (α-Me ether) with H<sub>2</sub>-Pd-C in MeOH at 50—55° gives 3 : 4-dimethoxy-o-toluidic acid, m.p. 95—96° (Me ester, m.p. ~30°, b.p. 156—157°/17 mm.), and meconine. In boiling HBr, (II) gives (45 min.) 3 : 4-dihydroxy-α-phthalidylacetic acid, +H<sub>2</sub>O, m.p. 228—229° (decomp.), and anhyd. R. S. C.

**Synthesis of anthracene-9 : 10-dicarboxylic acid.** H. Beyer and H. Fritsch (*Ber.*, 1941, 74, [B], 494—499).—9 : 10-Dibromoanthracene (I) and CuCN in boiling quinoline give 9 : 10-dicyanoanthracene, m.p. 328—330°, hydrolysed (conc. H<sub>2</sub>SO<sub>4</sub> at 100°) to anthracene-9 : 10-dicarboxylamide, m.p. 342—345° (decomp.) (does not give the acid with HNO<sub>3</sub>). (I) and Mg (activated by EtBr) in Bu<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> followed by CO<sub>2</sub> afford 9-bromoanthracene-10-carboxylic acid, m.p. 273° [Me (by CH<sub>2</sub>N<sub>2</sub> only), m.p. 114—115°, and Et (by CHMeN<sub>2</sub>), m.p. 83°, ester; 1 : 1-adduct, m.p. 265° (decomp.), with (CH<sub>3</sub>CO)<sub>2</sub>O], reduced (2 H<sub>2</sub>, PtO<sub>2</sub>, AcOH, room temp.) to the 1 : 2 : 3 : 4-H<sub>4</sub>-derivative. Schlenk's method (A., 1914, i, 398) gives 9 : 10-dihydroanthracene-9-carboxylic, m.p. 206—207° [Me, m.p. 98—99° (lit.

84—95°), and *Et*, m.p. 54—55°, ester; *hydrazide*, m.p. 206—207°, and -9:10-dicarboxylic acid (I), m.p. 305—307° (decomp.) [*Me*, m.p. 163—164° (clear at 165°), and *Et*, m.p. 68—69° (clear at 70°), ester; *dihydrazide*, m.p. 310—312° (decomp.) (block)]. *Se* and (I) at 300° give anthracene but (II) at 220—230° affords *Me*, anthracene-9:10-dicarboxylate, m.p. 180—181°, hydrolysed (boiling 20% *MeOH-KOH*) to the acid, m.p. ~341—342° (decomp.).

H. B.

**Stereochemistry of inner complex copper salts.** P. Pfeiffer and H. Krebs (*J. pr. Chem.*, 1940, [ii], 155, 77—114).—Attempts to decide the configuration by preparing *cis-trans* isomeric or optically active 4-covalent Cu compounds failed. A planar configuration is favoured. Cu salicylaldehydemethylimine, dimorphic (green needles; black rhombic pyramids), m.p. 158°, is obtained from (a) *o*-OH·C<sub>6</sub>H<sub>4</sub>·CHO (I), Cu(OAc)<sub>2</sub>, and NH<sub>2</sub>Me in EtOH at room temp. (96% yield) and (b) from Cu salicylaldehyde (II) and NH<sub>2</sub>Me in boiling EtOH; the brown (A., 1939, II, 479) or other form could not be isolated. Cu salicylaldehydeanil, m.p. 234—236° (Schiff, *Annalen*, 1869, 150, 197), is similarly obtained by both methods in only one form. Cu salicylaldehyde-*p*-nitroanil, +C<sub>5</sub>H<sub>5</sub>N and anhyd., m.p. 309° (decomp.), and -*a*-naphthylimine, m.p. 241.5°, are obtained by method (b). 2:1-OH·C<sub>10</sub>H<sub>6</sub>·CHO, Cu(OAc)<sub>2</sub>, and NH<sub>2</sub>R in EtOH give Cu 2-hydroxy-1-naphthaldehyde-methyl- (III), m.p. 235°, and -1'-naphthyl-imine, m.p. 269—270°, and -anil, m.p. 238—239° [also obtained from (1:2-CHO·C<sub>10</sub>H<sub>6</sub>·O)<sub>2</sub>Cu and NH<sub>2</sub>Ph in xylene at 150°] (cf. *loc. cit.*), which are also obtained in only one form [except for (III)]. *β*-Di-*o*-hydroxyanilo-*n*-butane, m.p. 232°, and benzilmono-*o*-hydroxyanil, +C<sub>5</sub>H<sub>5</sub>N, m.p. 90—120°, are obtained from *o*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH by Ac<sub>3</sub> in boiling EtOH and Bz<sub>2</sub> in boiling C<sub>6</sub>H<sub>5</sub>N, respectively, but give no Cu derivatives. *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and (II) in boiling C<sub>5</sub>H<sub>5</sub>N give the Cu, +C<sub>5</sub>H<sub>5</sub>N, salt of Cu salicylaldehyde-*p*-carboxyanil; the derived Na<sub>2</sub>, +9H<sub>2</sub>O and anhyd., and Ba salts are too unstable for attempts at resolution. *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>Na and (II) in boiling EtOH give the Na<sub>2</sub>, brownish-red and dark brown forms, both +5H<sub>2</sub>O and anhyd., and thence the Ba salts, brownish-red, +5H<sub>2</sub>O and anhyd., and dark brown, +9H<sub>2</sub>O and anhyd., all decomp. 350—370°, of Cu salicylaldehyde-*p*-sulphoanil; derived alkaloidal salts are intractable; adding 0.66 equiv. of *d*-(Co(NH<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·NH<sub>2</sub>)<sub>3</sub>)(SO<sub>4</sub>)<sub>3</sub> (IV) to the Ba salt gives a salt, +17H<sub>2</sub>O and anhyd., the [M] of which coincide with those of (IV) (as bromide). Hal·[CH<sub>2</sub>]<sub>2</sub>·NH<sub>2</sub>·HHal, (II), and NaOAc in boiling EtOH give Cu salicylaldehyde-*β*-chloro-, m.p. 168°, and -*β*-iodo-ethylimine, m.p. 143—144°, the halogen of which could not be exchanged for NMe<sub>2</sub>. Ni salicylaldehyde-*β*-chloroethylimine, m.p. 175—177°, is similarly prepared. NH<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·NEt<sub>2</sub> (V) and (II) give exothermally Cu salicylaldehyde-*β*-diethylaminoethylimine, green, m.p. 142°, but the di-imine could not be prepared. Warming (I) and (V) gives salicylaldehyde-*β*-diethylaminoethylimine, b.p. 168—172°/12 mm.; the derived methiodide, m.p. 148—149°, with Cu(OAc)<sub>2</sub> and anhyd. NaOAc in MeOH at 0° gives the Cu derivative dimethiodide, C<sub>22</sub>H<sub>14</sub>O<sub>2</sub>N<sub>4</sub>I<sub>2</sub>Cu, +1.5H<sub>2</sub>O and anhyd., m.p. 210—220° (decomp.; varies with rate of heating), which yields the dimetho-*d*-*α*-bromo-*π*-camphorsulphonate, green, +1.5H<sub>2</sub>O and anhyd., m.p. 240—245° (variable); pptn. of only 50% of the salt gives a substance, the [M] of which is due solely to the anion. Ni, m.p. 246—247° (in boiling 96% EtOH or moist COMe<sub>2</sub> gives *o*-OH·C<sub>6</sub>H<sub>4</sub>·CH·N·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub>·*p*, m.p. 134°, and Cu salicylaldehyde-*p*-dimethylaminoanil, sinters 206—207°, m.p. 208.5° (dimethiodide; dimetho-*α*-bromo-*π*-camphorsulphonate), are also prepared. 4:1-SO<sub>3</sub>H·C<sub>10</sub>H<sub>6</sub>·N<sub>2</sub>Cl and *p*-cresol in NaOH give Na *p*-cresol-3'-azo-1'-naphthalene-4'-sulphonate, decomp. ~300°, and thence, by way of the Ba salt, the acid, +H<sub>2</sub>O, which with Cu(OAc)<sub>2</sub> in boiling EtOH gives the Cu derivative (A; R = 4:1-SO<sub>3</sub>H·C<sub>10</sub>H<sub>6</sub>·), +6H<sub>2</sub>O (Na<sub>2</sub> salt, +6H<sub>2</sub>O, too dark for optical measurement). 4:2:1-NMe<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(OH)·N<sub>2</sub>Ph, Cu(OAc)<sub>2</sub>, and NaOAc in boiling MeOH give the Cu derivative [analogous to A, R = Ph], which is unstable and does not give quaternary salts. *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub>Cl (prep. from *p*-NHAc·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub>I described) is diazotised and coupled with *p*-cresol to give the salt, 2:5:1-OH·C<sub>6</sub>H<sub>3</sub>Me·N<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub>Cl·*p*, +1.5H<sub>2</sub>O, m.p. 200—210° (decomp.; varies with rate of heating); with Cu(OH)<sub>2</sub> in boiling EtOH this gives the Cu derivative (A; R = *p*-NMe<sub>2</sub>Cl·C<sub>6</sub>H<sub>4</sub>), sinters 185—190°, and thence the dimetho-*α*-bromo-*π*-camphorsulphonate, m.p. 223—224° (decomp.), which, when formed by half-pptn., has only very slight optical activity.

R. S. C.

**Androtermone of *Chlamydomonas eugametos*; 1-4-hydroxy-2:6:6-trimethyl- $\Delta^1$ -tetrahydrobenzaldehyde.** R. Kuhn and I. Löw (*Ber.*, 1941, 74, [B], 219—231).—Hydrolysis (dil. acid or alkali) of picrocrocin (I) to *d*-glucose (II) and 2:6:6-trimethyl- $\Delta^1$ : $\Delta^3$ -dihydrobenzaldehyde (safranal) (III) (A., 1934, 395) may occur in two stages with production of a hydroxyaldehyde and its subsequent dehydration. The reaction is now followed polarimetrically in 50 vol.-% EtOH since (III) is insol. in H<sub>2</sub>O. Reliable observations are not obtained for alkaline hydrolysis as (II) is largely destroyed at the necessary [OH] but alkaline hydrolysis is best for prep. of (III). Hydrolysis with HCl is unimol. with energy of activation 7590 g.-cal. per mol. between 29.9° and 19.5° and 11,380 g.-cal. per

mol. between 19.5° and 9°. No indication of the accumulation of an intermediate product was observed. (I) is a  $\beta$ -glucoside since emulsin at pH 6.0 and 27° affords 4-hydroxy-2:6:6-trimethyl- $\Delta^1$ -tetrahydrobenzaldehyde (IV), b.p. 80—90° (bath)/0.001 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> -84.2° and -87.2° in 96% EtOH. The thiosemicarbazone, m.p. 191—192°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -64° in 96% EtOH (absorption band in EtOH at 305 m $\mu$ ), of (IV) is hydrolysed by 2N-H<sub>2</sub>SO<sub>4</sub> to (III), b.p. ~60°/0.001 mm. [thiosemicarbazone, m.p. 191° (decomp.)], shows an absorption band in EtOH at 340 m $\mu$ . Comparison of the optical inactivation of (IV) by acid with hydrolysis of (I) shows that these proceed at the same rate, indicating that the latter process does not involve (IV). The termone activity of (IV) is ten times that of (III), the abs. activity being 1.3 mols. per cell, and it is concluded that 1 mol. suffices to convert a hermaphrodite cell into a male cell. J. WA.

**Synthesis of 3-hydroxy-4-methoxy- (homoisovanillin) and 3:4-dihydroxy-phenylacetaldehyde (homoprotocatechnaldehyde).** C. Schöpf, (Miss) E. Brass, E. Jacobi, W. Jorde, W. Mocnik, L. Neuroth, and W. Salzer (*Annalen*, 1940, 544, 30—62).—Methods of synthesising CH<sub>2</sub>Ar·CHO are discussed; some are investigated. The mixture obtained from commercial eugenol Me ether (I) by MgMeI (Hirao, A., 1936, 839), with KOH-EtOH at 0° gives the insol. K salt and thence the benzoate, m.p. 67° (lit. 69°), of eugenol; the crude chavibetol (II) in the filtrate is purified by means of the benzoate, m.p. 49.5°, which yields pure (II), b.p. 124°/12 mm. Chavibetol CH<sub>2</sub>Ph ether (III), m.p. 48°, is obtained from pure or, in better over-all yield, crude (II) by CH<sub>2</sub>PhCl and K<sub>2</sub>CO<sub>3</sub> in boiling MeOH. 3:4:1-CH<sub>2</sub>Ph·O·C<sub>6</sub>H<sub>3</sub>(OMe)·CH<sub>2</sub>·CO<sub>2</sub>H with PCl<sub>5</sub>—or, less well, pure SOCl<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> gives the chloride, which with CH<sub>2</sub>N<sub>2</sub>-Et<sub>2</sub>O at 0° and then room temp. gives 3-benzyloxy-4-methoxybenzyl CHN<sub>2</sub> ketone, m.p. 86°, converted in AcOH at 60—70° (finally 100°) into the CH<sub>2</sub>·OAc ketone (77%), m.p. 106°. When boiled with Al(OPr<sup>i</sup>)<sub>3</sub>-Pr<sup>i</sup>OH with removal of COMe<sub>2</sub>, this gives  $\gamma$ -3-benzyloxy-4-methoxyphenylpropane- $\alpha\beta$ -diol (IV) (94%), m.p. 110°, which is also obtained by treating AgOBz with I and then (III) in boiling C<sub>6</sub>H<sub>6</sub> (absence of H<sub>2</sub>O) and hydrolysing the product by NaOH-MeOH. With H<sub>2</sub>-Pd-BaSO<sub>4</sub>, (IV) gives  $\alpha$ -3-hydroxy-4-methoxyphenylpropane- $\alpha\beta$ -diol (chavibetol glycol), m.p. 88°, which could not be converted into CH<sub>2</sub>Ar·CHO. The azlactone from 3:4:1-CH<sub>2</sub>Ph·O·C<sub>6</sub>H<sub>3</sub>(OMe)·CHO with 10% NaOH-N<sub>2</sub> gives 3:4:1-CH<sub>2</sub>Ph·O·C<sub>6</sub>H<sub>3</sub>(OMe)·CH<sub>2</sub>·CO·CO<sub>2</sub>H (V), m.p. 159°, reduced by H<sub>2</sub>-PtO<sub>2</sub> and then -Pd-BaSO<sub>4</sub> in MeOH to 3:4:1-OH·C<sub>6</sub>H<sub>3</sub>(OMe)·CH<sub>2</sub>·CH(OH)·CO<sub>2</sub>H (VI), sinters 167°, m.p. 170°, whence no aldehyde could be obtained. The Me ester (prep. by CH<sub>2</sub>N<sub>2</sub>), m.p. 148—150°, of (V) gives similarly the Me ester, m.p. 62°, of (VI). Zn dust reduces (V) in 50% AcOH to  $\alpha$ -hydroxy- $\beta$ -3-benzyloxy-4-methoxyphenylpropionic acid, m.p. 129—130°; the Me ester, m.p. 87°, of which with MgMeI-Et<sub>2</sub>O and then conc. aq. NH<sub>4</sub>Cl gives  $\alpha$ -3-benzyloxy-4-methoxyphenylisopentane- $\beta\gamma$ -diol (VII), m.p. 86°. Pb(OAc)<sub>4</sub> oxidises (IV) or (VII) to 3-benzyloxy-, b.p. 155° (bath)/0.01 mm. (semicarbazone, m.p. 143—144°; 2:4-dinitrophenylhydrazone, m.p. 151—152°), hydrogenated (Pd; MeOH) to PhMe, and 3-hydroxy-4-methoxyphenylacetaldehyde, b.p. 110—115° (bath)/0.05 mm. (semicarbazone, m.p. 182—183°), which is stable at pH 3—4, fairly stable at pH 5—6, but unstable at pH 8. When (I) or, less well, eugenol or safrole is heated with an excess of MgMeI-xylene-N<sub>2</sub> at 160—180°, the mixture contains 33% of 3:4:1-(OH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CH<sub>2</sub>·CH·CH<sub>2</sub>, m.p. 47—58° (diacetate, b.p. 150—160° (bath)/12 mm., with O<sub>3</sub> gives no CH<sub>2</sub>Ar·CHO). CH<sub>2</sub>PhCl-K<sub>2</sub>CO<sub>3</sub>-COMe<sub>2</sub>-N<sub>2</sub> then gives 3:4-dibenzyloxyallylbenzene (75%), m.p. 37—38°, purified by chromatography (AlO<sub>3</sub>; C<sub>6</sub>H<sub>6</sub>) and fractional freezing in MeOH and converted by AgOBz-I-C<sub>6</sub>H<sub>5</sub> and then NaOH-MeOH-H<sub>2</sub>O into  $\gamma$ -3:4-dibenzyloxyphenylpropane- $\alpha\beta$ -diol (75%), m.p. 82—83°, and thence [Pb(OAc)<sub>4</sub>] into 3:4-dibenzyloxy- (75%), decomposes at 0.01 mm. (semicarbazone, m.p. 158°), and (activated PdO  $\rightarrow$  Pd-H<sub>2</sub>-MeOH) 3:4-dihydroxy-phenylacetaldehyde (VIII) (semicarbazone, m.p. 200—201°). Under certain conditions (VIII) polymerises, as formed, in presence of the catalyst. In H<sub>2</sub>O, (VIII) gives a violet colour with Schiff's reagent, a green colour with FeCl<sub>3</sub>, and an orange-red colour with HIO<sub>4</sub> (stable *o*-quinone formed), reduces AuCl<sub>3</sub>, cold NH<sub>3</sub>-AgNO<sub>3</sub>, and hot neutral AgNO<sub>3</sub>. Its 2:4-dinitrophenylhydrazone, m.p. 169—170°, is unstable in acid; the *p*-nitro- and *p*-bromo-phenylhydrazones are too unstable to be isolated. Its stability decreases from pH 3—4 to pH 7—8. 3:4:1-CH<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·CH<sub>2</sub>·CO·CO<sub>2</sub>H (IX) with H<sub>2</sub>-PtO<sub>2</sub> in aq. Na<sub>2</sub>CO<sub>3</sub> gives  $\alpha$ -hydroxy- $\beta$ -3:4-methylenedioxyphenylpropionic acid (X), m.p. 101°, which with Pb(OAc)<sub>4</sub> gives CO<sub>2</sub> and only 31—34% of homopiperonal (XI). The Me ester, m.p. 130—131°, of (IX) in MeOH yields similarly the Me ester, m.p. 39°, of (X), converted by an excess of MgMeI into  $\alpha$ -3:4-methylenedioxyphenylisopentane- $\beta\gamma$ -diol, m.p. 106°, which with Pb(OAc)<sub>4</sub> in C<sub>6</sub>H<sub>6</sub> gives good yields of (XI) and COMe<sub>2</sub>. 3:4:1-(OAc)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CH<sub>2</sub>·CH·CH<sub>2</sub>, b.p. 99°/0.06 mm., with BzO<sub>2</sub>H in CHCl<sub>3</sub> gives an oil, but the 2:3-(OAc)<sub>2</sub> compound, m.p. 65°, at 0° and then room temp. gives after 5 days ~50% of 2:3-diacetoxy- $\beta\gamma$ -epoxy-*n*-propylbenzene, m.p. 86°. 4-Acetoxy-3-methoxy- $\beta\gamma$ -epoxy-*n*-propylbenzene (similarly prepared), m.p. 50—52°, b.p. 133°/0.05 mm., in boiling 10% AcOH gives 3:4:1-OMe·C<sub>6</sub>H<sub>3</sub>(OAc)·CH<sub>2</sub>·CH(OH)·CH<sub>2</sub>·OH, b.p. 168°/0.03 mm. 3:4:1-(CH<sub>2</sub>Ph·O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO (improved prep.; 73% yield), m.p.

92—93°, gives the *azlactone*, m.p. 156—157°, which with alkali yielded no pyruvic acid. Br converts *isoferric acid* in AcOH or its acetate in  $\text{CHCl}_3$  into *ω-bromo-3-hydroxy-*, m.p. 95—96°, or *-3-acetoxy-4-methoxystyrene*, m.p. 101—102°, respectively. 3:4:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CH:CHBr and NaOEt at 180—185° give 3:4:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·C:CH, m.p. 73—74°, b.p. 130°/15 mm. 3:4:1-(OAc)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO·CH<sub>2</sub>·OAc and Zn dust in AcOH at 70° give 3:4:1-(OAc)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·COMe, m.p. 86° (2:4-dinitrophenylhydrazones, m.p. 192—193°) (cf. Voswinckel, A., 1910, i, 42; Birnbaum *et al.*, A., 1939, II, 373).

R. S. C.

**Influence of alkylation on reactions of acid derivatives in the Friedel-Crafts synthesis.** E. Rothstein and M. A. Saboor (*J.C.S.*, 1943, 425—429).—Mechanisms are suggested for the two classes of reactions of acids or their chlorides or anhydrides and  $\text{AlCl}_3$  or  $\text{P}_2\text{O}_5$ , where the product is either a ketone or an unsaturated substance. The absence of an ionisable α-H leads to the formation of an unsaturated substance, usually polymerised, with loss of CO; in other cases, little CO is eliminated and a ketone results. Dry distillation of (CPhMe<sub>2</sub>·CMe<sub>2</sub>·CO<sub>2</sub>)<sub>2</sub>Ca gives, with loss of CO and H<sub>2</sub>O, an unsaturated hydrocarbon, C<sub>12</sub>H<sub>16</sub>, b.p. 110°; a second hydrocarbon, C<sub>12</sub>H<sub>16</sub>, b.p. 154°, is obtained by distillation of the acid with soda-lime. Normal reaction of acid derivatives with  $\text{AlCl}_3$  and C<sub>6</sub>H<sub>6</sub> is possible only where an α-H is present, and the aromatic nucleus will attach itself to the CO group nearest to the one which is most ionised. The sole product from trimethylsuccinic anhydride,  $\text{AlCl}_3$ , and C<sub>6</sub>H<sub>6</sub> is β-benzoyl-αα-dimethyl-n-butyric acid (I), m.p. 135.6° (or γ-hydroxy-γ-phenyl-ααβ-trimethylbutyrolactone) [Me ester (or ether), b.p. 151°/8 mm.; excess of AcCl gives γ-phenyl-ααβ-trimethyl-Δ<sup>β</sup>-butenolactone, b.p. 145°/10 mm.; HI affords γ-phenyl-ααβ-trimethylbutyrolactone, m.p. 71°], also obtained by methylation (Me-KOBU<sup>r</sup>) of the Me ester, b.p. 153°/7 mm., m.p. 46—47° (2:4-dinitrophenylhydrazones, m.p. 126°), of CPh·CH<sub>2</sub>·CMe<sub>2</sub>·CO<sub>2</sub>H (II), m.p. 173° (2:4-dinitrophenylhydrazones, m.p. 198—199°). (II) is reduced (AcOH-HI-red P) to Ph·[CH<sub>2</sub>]<sub>2</sub>·CMe<sub>2</sub>·CO<sub>2</sub>H. Excess of AcCl converts (II) into γ-phenyl-αα-dimethyl-Δ<sup>β</sup>-butenolactone, m.p. 45°. Attempted synthesis of CPh·CMe<sub>2</sub>·CHMe·CO<sub>2</sub>H by methylation of CPh·CMe<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>H, m.p. 101—102° (Me ester, b.p. 131—143°/8 mm.), failed. Methylation of the Me ester, b.p. 164°/14 mm., of β-benzoyl-α-methyl-n-butyric acid, m.p. 78—79° [obtained from trans-(CHMe·CO)<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub>, and  $\text{AlCl}_3$  at b.p., then at 100°], also gives (I). A ketone or CO-acid is not obtained by Friedel-Crafts reaction on the anhydrides or chlorides of *tert.*-acids. (CMe<sub>2</sub>·CO)<sub>2</sub>O and C<sub>6</sub>H<sub>6</sub>— $\text{AlCl}_3$  at 0°, then gradually to 100°, give CO (60% yield in the cold), a neutral substance, C<sub>20</sub>H<sub>22</sub>O<sub>2</sub>, m.p. 147—148°, and (mainly) β-phenyl-ααβ-trimethyl-n-butyric acid (III), m.p. 179° [Me ester, m.p. 24—25° (Ag salt and Me)], or from CH<sub>2</sub>·CMe·CMe<sub>2</sub>·CO<sub>2</sub>Me—C<sub>6</sub>H<sub>6</sub>— $\text{AlCl}_3$ ; anhydride, m.p. 87°; NO<sub>2</sub>-derivative, m.p. 232°, also obtained through its Et ester, b.p. 138°/11 mm., from Et β-chloro-ααβ-tetramethylpropionate, b.p. 70—74°/8 mm. (from the OH-ester and  $\text{SOCl}_2$ ·C<sub>5</sub>H<sub>5</sub>N), and from the β-OH-ester. (III) and conc. H<sub>2</sub>SO<sub>4</sub> yield 2:2:3:3-tetramethyl-α-hydrindone, b.p. 142°/25 mm. (NO<sub>2</sub>-derivative, m.p. 130—131°). β-p-Tolyl-ααβ-trimethyl-n-butyric acid has m.p. 178°. CH<sub>2</sub>·CH·CMe<sub>2</sub>·CO<sub>2</sub>Me— $\text{AlCl}_3$ —C<sub>6</sub>H<sub>6</sub> afford, through the Me ester, b.p. 124—126°, β-phenyl-αα-dimethyl-n-butyric acid, m.p. 54—57°. (Bu<sup>r</sup>CO)<sub>2</sub>O (from the chloride and dry K or Ag salt at 100°) and C<sub>6</sub>H<sub>6</sub>— $\text{AlCl}_3$  afford PhBu<sup>r</sup> (55% yield), Bu<sup>r</sup>CO<sub>2</sub>H, and CO. COCl·CMe<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Me (Friedel-Crafts) gives (II), and (III) is similarly obtained from COCl·[CMe<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>Me. Impure (?) CPh·CMe<sub>2</sub>·CHMe·CO<sub>2</sub>H (Me ester, b.p. 95°/0.3 mm.) is probably obtained from CPhPr<sup>β</sup> (K derivative) and CHMeI·CO<sub>2</sub>Et. Condensation of CPh·CMe<sub>2</sub>Br with CMeNa(CO<sub>2</sub>Et)<sub>2</sub> or CN·CHNa·CO<sub>2</sub>Et, or of CPhPr<sup>β</sup> (Na or K derivative) with CHBr(CO<sub>2</sub>Et)<sub>2</sub> was not successful.

A. T. P.

#### Action of sodium on ethyl β-methylbutane-αβδ-tricarboxylate.

**I. [Structure of the methylated condensation product.] II. Structure of the ethylated condensation product.** R. N. Chakravarti (*J. Indian Chem. Soc.*, 1943, 20, 173—177, 189—194).—I. The CO<sub>2</sub>Et concerned in the Dieckmann cyclisation of CO<sub>2</sub>Et·CH<sub>2</sub>·CH<sub>2</sub>·CMe(CO<sub>2</sub>Et)·CH<sub>2</sub>·CO<sub>2</sub>Et (I) is that on C<sub>(α)</sub>, and not that on C<sub>(δ)</sub>, as stated by Baker (A., 1931, 957). (I) with Na in C<sub>6</sub>H<sub>6</sub> and then MeI (*in situ*) gives Et<sub>2</sub> 3:5-dimethylcyclopentanone-3:5-dicarboxylate (II), b.p. 135°/6 mm. (no colour with FeCl<sub>3</sub>), hydrolysed (KOH—25% EtOH) to β-methylpentane-αβδ-tricarboxylic acid (III), m.p. 178—179° (p-phenylphenacyl ester, m.p. 158°). (II) with boiling NaOEt—EtOH gives the Et<sub>2</sub> ester, b.p. 140—142°/5 mm., of (III), which with Na in C<sub>6</sub>H<sub>6</sub> gives Et<sub>2</sub> 2:4-dimethylcyclopentanone-4:5-dicarboxylate, b.p. 130—133°/6 mm. (violet colour with FeCl<sub>3</sub>). Hydrolysis with 6% HCl then gives 2:4-dimethylcyclopentanone-4-carboxylic acid, an oil [semicarbazone, m.p. 173° (decomp.)]. CH<sub>2</sub>Ac·CHMe·CO<sub>2</sub>Et, CN·CH<sub>2</sub>·CO<sub>2</sub>Et, and NH<sub>2</sub>Ac in AcOH (cf. Cope, A., 1938, II, 5) give Et<sub>2</sub> α-cyano-β-methyl-Δ<sup>α</sup>-pentene-αδ-dicarboxylate, b.p. 148°/5 mm., which with HCN affords Et<sub>2</sub> αβ-dicyano-β-methylpentane-αδ-dicarboxylate, b.p. 176°/5 mm., hydrolysed (conc. HCl) to (III).

II. (I) with Na in C<sub>6</sub>H<sub>6</sub> and then EtI (*in situ*) gives Et<sub>2</sub> 3-methyl-5-ethylcyclopentanone-3:5-dicarboxylate (IV), b.p. 142°/6 mm. (no colour with FeCl<sub>3</sub>), hydrolysed (KOH—25% EtOH) to β-methyl-

n-hexane-αβδ-tricarboxylic acid (V), m.p. 172—173°. Ketonic hydrolysis of (IV) gives 3-methyl-5-ethylcyclopentanone-3-carboxylic acid (VI) [semicarbazone, m.p. 191° (decomp.)]; Et ester, b.p. 110°/8 mm. (semicarbazone, m.p. 142—143°). Baker (*loc. cit.*) represented (V) as γ-methyl-n-hexane-αγδ-tricarboxylic acid (VII). (VII) was synthesised from CO<sub>2</sub>Et·[CH<sub>2</sub>]<sub>2</sub>·CMe(CN)·CH(CN)·CO<sub>2</sub>Et (Banerjee, A., 1941, II, 16) by ethylation with NaOEt and EtI to Et<sub>2</sub> γδ-dicyano-γ-methylhexane-αδ-dicarboxylate, b.p. 175°/5 mm., followed by hydrolysis with conc. HCl; it has m.p. 169°, depressed when mixed with (V). The Et<sub>2</sub> ester, b.p. 150°/5 mm., of (VII) with Na in C<sub>6</sub>H<sub>6</sub> gives Et<sub>2</sub> 3-methyl-2-ethylcyclopentanone-3:5-dicarboxylate, b.p. 150°/8 mm. (violet colour with FeCl<sub>3</sub>), hydrolysed by 6% HCl to 3-methyl-2-ethylcyclopentanone-3-carboxylic acid, m.p. 91° [semicarbazone, m.p. 213—214° (decomp.)]. CH<sub>2</sub>Ac·CHEt·CO<sub>2</sub>Et, CN·CH<sub>2</sub>·CO<sub>2</sub>Et, NH<sub>2</sub>Ac, and AcOH give Et<sub>2</sub> α-cyano-β-methyl-Δ<sup>α</sup>-hexene-αδ-dicarboxylate, b.p. 150°/5 mm.; addition of HCN and hydrolysis (conc. HCl) of the resulting Et<sub>2</sub> αβ-dicyano-β-methylhexane-αδ-dicarboxylate, b.p. 170°/4 mm., affords (V). The Et<sub>2</sub> ester b.p. 140°/5 mm., of (V) with Na in C<sub>6</sub>H<sub>6</sub> gives Et<sub>2</sub> 3-methyl-5-ethylcyclopentanone-2:3-dicarboxylate, b.p. 130°/5 mm. (violet colour with FeCl<sub>3</sub>), hydrolysed by 6% HCl to (VI).

S. A. M.

**Syntheses in the sterol and sex hormone group. IV. Synthesis of 3-β-naphthylcyclopentanone derivatives.** C. K. Chuang, J. H. Chu, and Y. S. Kao (*Ber.*, 1941, 74 [B], 798—806).—2-C<sub>18</sub>H<sub>7</sub>·CO·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>Et, CH<sub>2</sub>Br·CO<sub>2</sub>Et, and Zn in C<sub>6</sub>H<sub>6</sub> give Et<sub>2</sub> β-hydroxy-β-2-naphthyladipate (I), m.p. 84—88° [and acidic products from which is obtained by hydrolysis (aq. KOH) a small amount of a β-2-naphthylidihydromuconic acid (II), m.p. 186—187°], which could not be dehydrated by  $\text{SOCl}_2$ —Et<sub>2</sub>O, Ac<sub>2</sub>O, or  $\text{P}_2\text{O}_5$ —C<sub>6</sub>H<sub>6</sub>. Hydrolysis (20% KOH at room temp.) of (I) gives β-hydroxy-β-2-naphthyladipic acid (III), m.p. 156—158° (decomp.) (p-nitrobenzyl ester, m.p. 132—133°), converted at 160—170° or by 6N-H<sub>2</sub>SO<sub>4</sub> in boiling CMe<sub>2</sub> into the γ-lactonic acid, m.p. 167—168°. Hydrolysis of (I) with boiling EtOH—KOH affords a little (III) and a mixture (A) of unsaturated acids from which (II) is isolable. (II) [also obtained in poor yield from (III) and boiling  $\text{Ac}_2\text{O}$ ] and (A) are reduced (H<sub>2</sub>, Pt-black, AcOH) to β-2-naphthyladipic acid (IV), m.p. 168—169° (p-nitrobenzyl ester, m.p. 98°). The Me<sub>2</sub> ester of (IV) gives (Dieckmann) 3-β-naphthylcyclopentanone [semicarbazone, m.p. 199—201° (lit. 196—197°)].

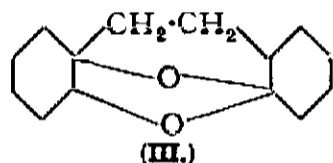
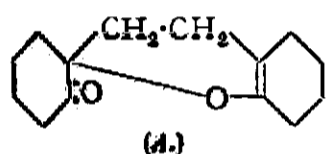
H. B.

**Reactions catalysed by aluminium chloride. XXI. Route to 8-methylhydrindan-1-one.** C. D. Nenitzescu and V. Przemetzky (*Ber.*, 1941, 74, [B], 676—686).—cycloHexene (I) and CH<sub>2</sub>Cl·OAc (II) in CS<sub>2</sub> at room temp. give 2-chlorohexahydrobenzyl acetate (III), b.p. 110—112°/14 mm. (the Cl is unaffected by boiling quinoline, NPhEt<sub>2</sub>, or EtOH—KOH, by KOAc at 200°, or by reducing agents), which with C<sub>6</sub>H<sub>6</sub>— $\text{AlCl}_3$  at 45° affords 4-phenylhexahydrobenzyl acetate, b.p. 156—158°/12 mm. (I), 37% CH<sub>2</sub>O—HCl (1 mol.), and ZnCl<sub>2</sub> at 0—45° give 2-chlorohexahydrobenzyl alcohol (IV), b.p. 105—107°/15 mm.; 2-bromohexahydrobenzyl alcohol, b.p. 120°/15 mm., and 2-chlorocyclopentylcarbinol, b.p. 92—93°/15 mm., are similarly prepared. (IV) with Na—H<sub>2</sub>O—Et<sub>2</sub>O affords hexahydrobenzyl alcohol, b.p. 182—185°/760 mm., and with Na—EtOH gives the 2-OEt-alcohol, b.p. 75°/10 mm., oxidised (aq. KOH—KMnO<sub>4</sub>) to 2-ethoxyhexahydrobenzoic acid, m.p. 96°. (III) and (IV) with solid KOH at 160° give Δ<sup>1</sup>-tetrahydrobenzyl alcohol (V), b.p. 90—93°/23 mm., attempted dehydrogenation (Cu at 300°) of which affords hexahydrobenzaldehyde. (I), 35% CH<sub>2</sub>O, and conc. H<sub>2</sub>SO<sub>4</sub> give the CH<sub>2</sub>: ether, b.p. 63—67°/10 mm., of 2-hydroxymethylcyclohexanol; this is unchanged by dil. acids at 150° or by Al<sub>2</sub>O<sub>3</sub> at 400°. 1-Methyl-Δ<sup>1</sup>-cyclohexene and (CH<sub>2</sub>O)<sub>x</sub> in AcOH—conc. H<sub>2</sub>SO<sub>4</sub> afford 2-methyl-Δ<sup>1</sup>-tetrahydrobenzyl acetate, b.p. 95—100°/18 mm., and some of the corresponding glycol diacetate; hydrolysis (20% NaOH) of the mixture gives 2-methyl-Δ<sup>1</sup>-tetrahydrobenzyl alcohol (VI), b.p. 106—108°/20 mm., and the glycol [yields (VI) when distilled with p-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>H]. The bromide from (VI) and PBr<sub>3</sub> is converted through the malonate, b.p. 162°/15 mm. (prep. in xylene at 120°), into β-2-methyl-Δ<sup>1</sup>-cyclohexenylpropionic acid, b.p. 162°/18 mm., and thence (chloride, b.p. 112—115°/9 mm., with  $\text{AlCl}_3$  in cyclohexane) into 8-methylhydrindan-1-one, b.p. 98—99°/15 mm., m.p. 39.5° (lit. 34° and an oil) [semicarbazone, forms, m.p. 214.5° and 224° (cf. lit.)], together with a little 8-methyltetrahydroindan-1-one (semicarbazone, m.p. 238°). β-Δ<sup>1</sup>-cycloHexenylpropionic acid, b.p. 156—159°/18 mm. (p-bromophenacyl ester, m.p. 112°) [similarly obtained starting with (V)], is similarly converted into 4:5:6:7-tetrahydroindan-1-one, b.p. 124—125°/17 mm. (semicarbazone, m.p. 243°). cycloHexanone, Cl·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>Et (or Br-ester), and Li in C<sub>6</sub>H<sub>6</sub> give (after hydrolysis) mono- and di-cyclohexylidenecyclohexanone and β-2-ketocyclohexylpropionic acid, b.p. 180—182°/15 mm., reduced (Na—Hg, H<sub>2</sub>O) to the 2-OH-acid lactone, b.p. 145—150°/? vac. CO<sub>2</sub>Me·[CH<sub>2</sub>]<sub>2</sub>·COCl, (I), and  $\text{AlCl}_3$  in PhNO<sub>2</sub> at room temp. afford Me γ-keto-γ-Δ<sup>1</sup>-cyclohexenylbutyrate, b.p. 170—175°/20 mm., the semicarbazone, m.p. 141.5°, of which with EtOH—NaOEt at 160° gives γ-Δ<sup>1</sup>-cyclohexenylbutyric acid, b.p. 165—167°/22 mm. This is cyclised (as above) to 1-keto-Δ<sup>8</sup>-octahydronaphthalene (semicarbazone, m.p. 241°). CMe<sub>2</sub>·CH<sub>2</sub> and (II) give γ-chloro-γ-methyl-n-butyl acetate, b.p. 112°/25 mm., whilst CH<sub>2</sub>:CH·CH<sub>2</sub>Cl,

$\text{CH}_3\text{Cl}\cdot\text{OMe}$ , and  $\text{ZnCl}_2$  afford  $\alpha\beta$ -dichloro-8-methoxy-n-butane, b.p.  $170^\circ/760$  mm., converted by boiling 10% KOH into  $\beta$ -chloro-8-methoxy- $\Delta^8$ -butene, b.p.  $42^\circ/18$  mm. H. B.

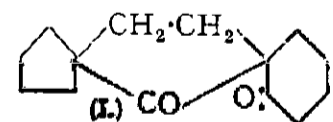
**Carbon rings. XXXII. Productive preparation of cyclononanone.** L. Ruzicka, P. A. Plattner, and H. Wild (*Helv. Chim. Acta*, 1943, 26, 1631—1637).—At room temp. the equilibrium cyclooctanonecyclohydrin (I)  $\rightleftharpoons$  cyclooctanone (II) + HCN lies almost entirely on the right side but at  $0^\circ$  (I) is obtained by the gradual addition of 37% HCl to an emulsion of (II) and KCN in  $\text{Et}_2\text{O}$  and is stabilised by conversion (well-cooled  $\text{Ac}_2\text{O}$  +  $\text{AcCl}$ ) into the acetate, b.p.  $94\text{—}100^\circ/0.25$  mm. This is hydrogenated ( $\text{PtO}_2$  in  $\text{AcOH}$  containing a little 37% HCl at  $60^\circ$ ) to cyclooctylmethylamine (III) and 1-acetoxycyclooctanecarboxylamide, m.p.  $109^\circ$ . Similar hydrogenation of (I) at  $18^\circ$  gives (III) (Bz derivative, m.p.  $69\text{—}70^\circ$ ), 1-aminomethylcyclooctanol (IV), m.p.  $35^\circ$  (hydrochloride, m.p.  $232^\circ$ ; N-Bz derivative, m.p.  $132.5\text{—}133^\circ$ ), and 1-hydroxycyclooctylmethyl-1'-hydroxycyclooctylmethylethylamine,  $[\text{CH}_2]_7\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\text{C}(\text{OH})\text{CH}_2)_7$ , b.p.  $140\text{—}142^\circ/0.1$  mm., m.p.  $105^\circ$ , converted by  $\text{Ac}_2\text{O}$  and  $\text{C}_5\text{H}_5\text{N}$  in  $\text{C}_6\text{H}_6$  into the monoacetate, m.p.  $95^\circ$ . (IV) is transformed by  $\text{HNO}_3$  into cyclononanone (V), b.p.  $94.5\text{—}95.5^\circ/13$  mm., m.p.  $34^\circ$ , purified through the semicarbazone, m.p.  $183^\circ$ . (V) is oxidised ( $\text{CrO}_3$  in  $\text{AcOH}$  at  $100^\circ$ ) to azelaic acid. M.p. are corr. H. W.

**"Dimeric 2-methylenecyclohexanone."** C. Mannich (*Ber.*, 1941, 74, [B], 557—564).—"Dimeric 2-methylenecyclohexanone" (I), b.p.  $160\text{—}161^\circ/14$  mm., is (A); it gives a mono-semicarbazone, m.p.  $206^\circ$ , and -oxime, m.p.  $123^\circ$  (cf. A., 1928, 300). With 20% HCl (I) gives 1-hydroxy-2 : 2'-diketo- $\alpha\beta$ -dicyclohexylethane, m.p.  $154\text{—}155^\circ$  [di-oxime, m.p.  $195^\circ$ , also obtained when (I) is treated with  $\text{NH}_2\text{OH}$  in weakly acid solution for a long time], which contains 1 active H and is reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{EtOH}$ ) to 1 : 2 : 2'-trihydroxy- $\alpha\beta$ -dicyclohexylethane, m.p.  $154^\circ$  (triacetate, m.p.  $71\text{—}72^\circ$ ). Similar reduction of (I) gives the alcohol (II) [(A) with  $\text{CH}_3\text{OH}$  for  $\text{CO}$ ], m.p.  $69\text{—}70^\circ$  (acetate, b.p.  $177\text{—}180^\circ/12$  mm.), converted by 20% HCl into the



diether (III), b.p.  $146\text{—}149^\circ/12$  mm. (II) and (III) are dehydrogenated ( $\text{Pt}$ -asbestos at  $320\text{—}330^\circ$  in  $\text{H}_2$ ) to ( $\alpha$ -OH- $\text{C}_6\text{H}_4\cdot\text{CH}_2$ ) $_2$ . (I), (II), or (III) with aq.  $\text{AcOH}\text{--}\text{CrO}_3$  at  $60^\circ$  gives  $\alpha$ -keto- $\alpha$ -2-ketocyclopentyl- $\gamma$ -1-hydroxy-2-ketocyclohexylpropane, m.p.  $134^\circ$ , cleaved by hot dil. KOH to cyclopentanone,  $\gamma$ -2-keto-2 : 3 : 4 : 6 : 7 : 8-hexahydro-1-naphthylbutyric acid (IV), m.p.  $111^\circ$  [semicarbazone, m.p.  $224^\circ$  (decomp.)], and  $\beta$ -1-hydroxy-2-ketocyclohexylpropionic acid lactone (V), m.p.  $60^\circ$  [semicarbazone, m.p.  $\sim 196^\circ$  (decomp.)]; oxime, m.p.  $124\text{—}125^\circ$ . Reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{EtOH}$ ) of (IV) affords  $\text{H}_4$ -[semicarbazone, m.p.  $\sim 209^\circ$  (decomp.)] or  $\text{H}_6$ -derivatives, m.p.  $147^\circ$ ; (IV) probably arises from the intermediate  $\epsilon$ -keto- $\eta$ -1-hydroxy-2-ketocyclohexyloctioic acid. Oxidation ( $\text{Ag}_2\text{O}$ ) of (V) gives  $\gamma$ -keto-azelaic acid reduced (Clemmensen) to azelaic acid. H. B.

**Rearrangement of "dimeric 2-methylenecyclohexanone" by acids.** C. Mannich (*Ber.*, 1941, 74, [B], 565—570).—"Dimeric 2-methylenecyclohexanone" or 1-hydroxy-2 : 2'-diketo- $\alpha\beta$ -dicyclohexylethane with boiling 20%  $\text{H}_2\text{SO}_4$  gives the diketone (I), b.p.  $155\text{—}156^\circ/10$  mm. (mono-semicarbazone, m.p.  $157\text{—}158^\circ$ , and -oxime, m.p.  $156\text{—}157^\circ$ ), reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{EtOH}$ ) to a CO-alcohol,  $\text{C}_{14}\text{H}_{22}\text{O}_2$ , b.p.  $162\text{—}163^\circ/12$  mm. (II) [oxime, m.p.  $198\text{—}199^\circ$ ; acetate (III), b.p.  $171\text{—}172^\circ/\text{vac.}$ ], or (exceptionally) an isomeric CO-alcohol, m.p.  $94\text{—}95^\circ$  (IV) (oxime, m.p.  $149\text{—}150^\circ$ ), also obtained from (III) and an excess of boiling N-EtOH-KOH. (II) or (IV) with Na-EtOH gives the glycol,  $\text{C}_{14}\text{H}_{24}\text{O}_2$ , m.p.  $169\text{—}170^\circ$  (diacetate, m.p.  $73^\circ$ ). Boiling 10% KOH converts (I) into 1- $\beta$ -2'-ketocyclohexylethylcyclopentane-1-carboxylic acid, m.p.  $84^\circ$  [semicarbazone, m.p.  $198^\circ$ ; p-nitrophenylhydrazone, m.p.  $156^\circ$  (decomp.)];  $\text{CHPh}$  derivative, m.p.  $126^\circ$ ], reconverted into (I) by  $\text{P}_2\text{O}_5$  at  $105^\circ$ , and oxidised ( $\text{KMnO}_4$ ; small amount) to  $\epsilon$ -keto- $\eta$ -1-carboxycyclopentyl-octioic acid, m.p.  $83^\circ$  [semicarbazone, m.p.  $171^\circ$  (decomp.)], or (large amount) to a mixture of  $\text{H}_2\text{C}_2\text{O}_4$ ,  $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , glutaric, adipic, 1-carboxycyclopentylacetic, and cyclopentane-1 : 1-dicarboxylic acid. H. B.



**Methylenequinones. Oxido-reductive dimerisation.** H. von Euler, E. Adler, and A. O. Caspersson (*Arkiv Kemi, Min., Geol.*, 1943, 16, A, No. 11, 14 pp.; cf. A., 1943, II, 189).—1 : 2 : 5- $\text{C}_6\text{H}_3\text{Me}(\text{OH})_2$ , 8% aq. NaOH, and 40%  $\text{CH}_2\text{O}$  (in  $\text{N}_2$ ) at  $2\text{—}5^\circ$  (70 hr.) give 2 : 5-dihydroxy-3-methylbenzyl alcohol (I), m.p.  $156.5\text{—}157.5^\circ$ ; its 2 : 5-Me $_2$  ether, m.p.  $74.5\text{—}75^\circ$ , is oxidised by aq.  $\text{KMnO}_4\text{--}\text{NaOH}$  to 2 : 5-dimethoxy-m-toluic acid, m.p.  $124\text{—}125^\circ$ , converted by  $\text{HBr}\text{--}\text{AcOH}$  into the 2 : 5-(OH) $_2$ -compound, m.p.  $\sim 190^\circ$  (decomp.) (lit.  $215^\circ$ ). Short treatment of (I) with HCl in  $\text{EtOAc}$  (solid  $\text{CO}_2$  cooling), followed by aq.  $\text{NaHCO}_3$ , gives, through the corresponding benzyl chloride (II), the unstable 1 : 6 : 4 : 2-O- $\text{C}_6\text{H}_2\text{Me}(\text{OH})_2\cdot\text{CH}_2$  (A), and thence a quinhydrone (III),  $\text{C}_{32}\text{H}_{32}\text{O}_8$ , m.p.  $210^\circ$  (pre-heated bath). (III) is reduced by  $\text{Zn}\text{--}\text{AcOH}$  (not by  $\text{SO}_2$  or  $\text{SnCl}_2$ ) to  $\alpha\beta$ -di-(2 : 5-dihydroxy-

3-methylphenyl)ethane (IV), m.p.  $286\text{—}287^\circ$  (pre-heated bath) (tetraacetate, m.p.  $167^\circ$ ), oxidised by  $\text{FeCl}_3$  in  $\text{MeOH}$  to the corresponding diquinone (V), m.p.  $193^\circ$ . (III) is synthesised from equal amounts of (IV) and (V) in  $\text{MeOH}$ . (II) is reduced by  $\text{Zn}$  dust in moist  $\text{Et}_2\text{O}$  or  $\text{C}_6\text{H}_6$  to (IV). (A) is considered to undergo oxido-reduction to 2 : 5 : 3 : 1-(OH) $_2\text{C}_6\text{H}_2\text{Me}\cdot\text{CH}_2\cdots$  and the corresponding quinone; the radicals then dimerise. A. T. P.

#### IV.—STEROLS AND STEROID SAPOGENINS.

**Oxidation of cholesterol and other unsaturated sterols in colloidal aqueous solution by molecular oxygen.** S. Bergström (*Arkiv Kemi, Min., Geol.*, 1943, 16, A, No. 10, 72 pp.).—An account of work previously abstracted (A., 1941, II, 139; 1942, II, 102, 230; 1943, II, 13).

**Cholesteryl thiocyanate.** A. Müller and E. Bályka (*Ber.*, 1941, 74, [B], 705—707).—Cholesteryl *p*-toluenesulphonate (I) or benzenesulphonate and KCNS in abs.  $\text{COMe}_2$  at  $100^\circ$  (sealed tube) give cholesteryl thiocyanate (II), m.p.  $128\text{—}129^\circ$ ,  $[\alpha]_D^{25} -14.6^\circ$  in  $\text{CHCl}_3$  (ct. lit.) (5 : 6-dibromide, m.p.  $79\text{—}80^\circ$ ,  $[\alpha]_D^{25} -34.6^\circ$  in  $\text{CHCl}_3$ ), converted by boiling  $\text{C}_6\text{H}_6\text{--}\text{N-MeOH}\text{--}\text{NaOMe}$  into dicholesteryl disulphide,  $[\alpha]_D^{25} -44.9^\circ$  in  $\text{CHCl}_3$ . Thermal rearrangement of (II) could not be effected. (II) or (better) (I) and boiling  $\text{NH}_2\text{Ph}$  give *N*-phenylcholesterylamine, m.p.  $189\text{—}190^\circ$ ,  $[\alpha]_D^{25} -35.6^\circ$  in  $\text{CHCl}_3$ , and [from (II)] a substance, m.p.  $>220^\circ$ . Cholesteryl chloride and NaI in  $\text{COMe}_2$  at  $180\text{—}190^\circ$  give  $\Delta^3,5$ -cholestadiene, m.p.  $77\text{—}78^\circ$ ,  $[\alpha]_D^{25} -80.2^\circ$  in  $\text{C}_6\text{H}_6$ . H. B.

**Acyl migration in the sterol series.** M. F. C. Paige (*J.C.S.*, 1943, 437—441).—Attempted partial hydrolysis of 3( $\beta$ ) : 6( $\beta$ )-diacetoxyl- $\Delta^4$ -cholestene to 6( $\beta$ )-acetoxyl- $\Delta^4$ -cholesten-3( $\beta$ )-ol failed. 3-O-Carbomethoxycholesterol (I) and aq.  $\text{SeO}_2\text{--}\text{Ac}_2\text{O}$  at  $105\text{—}110^\circ$  give 3-O-carbomethoxy-4-acetoxylcholesterol (II), m.p.  $160.5\text{—}161^\circ$ , hydrolysed by boiling 5% KOH-MeOH to *cis*- $\Delta^5$ -cholestene-3 : 4-diol (III). Oxidation of (I) with aq.  $\text{SeO}_2$  in  $\text{AcOH}$  at  $100^\circ$  gives (II) and the carbonate (IV), m.p.  $173\text{—}173.5^\circ$ , of (III); (IV) is also obtained from (III) and  $\text{PhMe}\text{--}\text{COCl}_2\text{--}\text{C}_5\text{H}_5\text{N}\text{--}\text{C}_6\text{H}_6$  at  $70^\circ$  (sealed tube). The 3 : 6-ester was not isolated in either oxidation of (I), but was probably present as hydrolysis of the non-cryst. residues gives a little  $\Delta^4$ -cholestene-3 : 6-diol. 4-Hydroxycholesterol and  $\text{ClCO}_2\text{Me}\text{--}\text{C}_5\text{H}_5\text{N}\text{--}\text{Et}_2\text{O}\text{--}\text{C}_6\text{H}_6$  at room temp. afford 4-hydroxy-3-O-carbomethoxycholesterol, m.p.  $157.5\text{—}159.5^\circ$  (benzoate, m.p.  $173\text{—}174^\circ$ ), acetylated ( $\text{Ac}_2\text{O}$ ) to (II), which is also obtained similarly from the 4-monoacetate of (III) and  $\text{ClCO}_2\text{Me}\text{--}\text{C}_5\text{H}_5\text{N}$ . 3-O-Carbomethoxycholesterol and aq.  $\text{SeO}_2\text{--}\text{Ac}_2\text{O}$  yield 3-O-carbomethoxy-4-acetoxylcholesterol (V), m.p.  $163\text{—}163.5^\circ$ , and 3-O-carbomethoxy-6-acetoxyl- $\Delta^4$ -cholesten-3-ol, m.p.  $121\text{—}122.5^\circ$  (hydrolysed to  $\Delta^4$ -cholestene-3 : 6-diol); the same products and (IV) are formed by oxidation in  $\text{AcOH}$ . (V) is hydrolysed to (III) and can be obtained from the 4-monoacetate of (III) and  $\text{ClCO}_2\text{Et}$ . (III) and  $\text{ClCO}_2\text{Et}\text{--}\text{C}_5\text{H}_5\text{N}$  afford 4-hydroxy-3-O-carbomethoxycholesterol, m.p.  $130.5\text{—}131^\circ$  (benzoate, m.p.  $131\text{—}131.5^\circ$ ), acetylated to (V). Acyl migration in the 3-monoesters of (III) probably occurs through the orthocarbonate. The 3-monoacetate and  $\text{EtCO}_2\text{H}$  at  $100^\circ$  afford some 4-acetate; even in  $\text{AcOH}$ , conversion is incomplete in 6 hr., indicating an equilibrium reaction. (IV) and  $\text{MeMgI}$  (in  $\text{Et}_2\text{O}\text{--}\text{dry H}_2$ ) give only  $\Delta^4$ -cholestene (VI). (I) is probably first oxidised in  $\text{AcOH}$  to its 4-OH derivative, which rearranges to an orthocarbonate; loss of  $\text{MeOH}$  then gives (IV). The 3-O- $\text{CO}_2\text{Me}$ - or - $\text{CO}_2\text{Et}$ -derivatives of (III) are converted by boiling  $\text{AcOH}$  or  $\text{EtCO}_2\text{H}$  into (IV). Hydrogenation ( $\text{Pd}$ , then  $\text{Pt}$ ) of 6( $\beta$ )-acetoxyl- $\Delta^4$ -cholesten-3-one gives a non-cryst. product, but Na- $\text{C}_5\text{H}_{11}\text{OH}$  followed by  $\text{BzCl}\text{--}\text{C}_5\text{H}_5\text{N}$  at room temp. yields cholestane-3( $\beta$ ) : 6( $\alpha$ )-diol dibenzoate, also obtained similarly from cholesterol  $\alpha$ - or  $\beta$ -oxide (modified prep.).  $\Delta^4$ -Cholestene-3 : 6-diol and boiling Na- $\text{C}_5\text{H}_{11}\text{OH}$  afford a hydrocarbon, m.p.  $79\text{—}80^\circ$ , possibly (VI). A. T. P.

**Constituents of the adrenal cortex and related substances. LXIV. Configurative connexion of 17( $\beta$ )-hydroxypregnane derivatives with glycerol grouping in the side-chain.** B. Koechlin and T. Reichstein (*Helv. Chim. Acta*, 1943, 26, 1328—1334).— $\Delta^5,17$ -Pregnadiene-3 : 21-diol diacetate is converted by  $\text{OsO}_4$  in  $\text{Et}_2\text{O}$  at room temp. followed by  $\text{Na}_2\text{SO}_3$  in boiling aq.  $\text{EtOH}$  and acetylation ( $\text{Ac}_2\text{O}\text{--}\text{C}_5\text{H}_5\text{N}$  at room temp.) into  $\Delta^5$ -pregnene-3( $\beta$ ) : 17( $\beta$ ) : 20( $\beta$ ) : 21-tetraol 3 : 20 : 21-triacetate, rhombs which pass into needles at  $184\text{—}185^\circ$  and melt at  $189\text{—}190^\circ$ ,  $[\alpha]_D^{25} +5.9^\circ \pm 1.5^\circ$  in  $\text{COMe}_2$ . It is hydrolysed by boiling KOH-MeOH to the tetraol (Prins records m.p.  $215\text{—}220^\circ$ , or  $220\text{—}223^\circ$  after prolonged keeping,  $[\alpha]_D^{25} -56.2^\circ \pm 5^\circ$  in  $\text{COMe}_2$ ), converted by  $\text{COMe}_2$  and anhyd.  $\text{CuSO}_4$  at room temp. into  $\Delta^5,20$  : 21-isopropylidenepregnene-3( $\beta$ ) : 17( $\beta$ ) : 20( $\beta$ ) : 21-tetraol, m.p.  $201\text{—}203^\circ$ , becomes opaque at  $100^\circ$ ,  $[\alpha]_D^{25} -62.7^\circ \pm 2^\circ$  in  $\text{COMe}_2$ . This is oxidised by  $\text{Al}(\text{OBu}^n)_3$  and  $\text{COMe}_2$  in boiling  $\text{C}_6\text{H}_6$  to  $\Delta^4,20$  : 21-isopropylidenepregnene-17( $\beta$ ) : 20( $\beta$ ) : 21-triol-3-one, two forms, m.p.  $146\text{—}147^\circ$  and  $200\text{—}204^\circ$  without change at  $147^\circ$ ,  $[\alpha]_D^{25} +74.7^\circ \pm 2^\circ$  in  $\text{COMe}_2$ , which is hydrolysed to  $\Delta^4$ -pregnene-17( $\beta$ ) : 20( $\beta$ ) : 21-triol-3-one (I), identified as the diacetate, m.p.  $196\text{—}197^\circ$ ,  $[\alpha]_D^{25} +135.9^\circ \pm 2^\circ$  in  $\text{COMe}_2$ , identical with that obtained from the  $\Delta^4$ -pregnene-17( $\beta$ ) : 20 : 21-triol-3-one of Ruzicka *et al.*

(A., 1939, II, 328). (I) is therefore configuratively similar to *allo*-pregnane-3( $\beta$ ):17( $\beta$ ):20( $\beta$ ):21-tetraol and  $\Delta^5$ -pregnene-3( $\beta$ ):17( $\beta$ ):20( $\beta$ ):21-tetraol. M.p. are corr. (block); limit of error  $\pm 2^\circ$ . H. W.

**Steroids and sex hormones. LXXXVI. Products of the hydrogenation of  $\Delta^{5:6-20:22}$ -3( $\beta$ )-hydroxynorcholadienoic acid.** P. A. Plattner and J. Pataki (*Helv. Chim. Acta*, 1943, 26, 1241—1252).—Further examples are given of the formation of isomerides due to differing configuration at C<sub>(20)</sub>. Those compounds which have a configuration at C<sub>(20)</sub> differing from that of cholesterol are termed 20-*iso*-derivatives. Me  $\Delta^{5:6-20:22}$ -3( $\beta$ )-acetoxynorcholadienoate is hydrogenated (Pt in AcOH) to Me 3( $\beta$ )-acetoxynorallochololate (I), m.p. 162.5—163°,  $[\alpha]_D^{25} + 11.7^\circ$  in CHCl<sub>3</sub>, hydrolysed to the 3( $\beta$ )-OH-acid, m.p. 225—226°,  $[\alpha]_D^{25} + 22.9^\circ$  in EtOH (Me ester, m.p. 157—158°,  $[\alpha]_D^{25} + 19.1^\circ$  in CHCl<sub>3</sub>), and a mixture which, after hydrolysis, gives 3( $\beta$ )-hydroxy-20-isonorallocholic acid, m.p. 249—251°,  $[\alpha]_D^{25} + 18.2^\circ$  in EtOH (Me ester, m.p. 169—171°,  $[\alpha]_D^{25} + 16.4^\circ$  in CHCl<sub>3</sub>), and its acetate, m.p. 135—137°,  $[\alpha]_D^{25} + 8.2^\circ$  in CHCl<sub>3</sub>).  $\Delta^{5:6-20:22}$ -3( $\beta$ )-Hydroxynorcholadienoic acid is hydrogenated (Raney Ni in aq. EtOH-NaOH) to  $\Delta^{5:6}$ -3( $\beta$ )-hydroxy-20-isonorcholenic acid, m.p. 263—264°,  $[\alpha]_D^{25} - 44.7^\circ$  in EtOH, and  $\Delta^{5:6}$ -3( $\beta$ )-hydroxynorcholenic acid (II), m.p. 244.5—245°,  $[\alpha]_D^{25} - 41.2^\circ$  in EtOH (Me ester, m.p. 143—145°,  $[\alpha]_D^{25} - 42.5^\circ$  in CHCl<sub>3</sub>), and its acetate, m.p. 132—134°. Hydrogenation of Me  $\Delta^{20:22}$ -3( $\beta$ )-acetoxynorallochololate (Pt in EtOH or AcOH) leads to (I); in presence of Raney Ni a mixture results containing predominatingly the 20-*iso*-form. Rapid addition of Me  $\Delta^{5:6}$ -3( $\beta$ )-acetoxychololate (III) in C<sub>6</sub>H<sub>6</sub> to MgMeBr in Et<sub>2</sub>O followed by alkaline hydrolysis gives  $\Delta^{5:6}$ -3( $\beta$ )-hydroxynorcholenyldimethylcarbinol, m.p. 181.5—182.5° (lit. 192°),  $[\alpha]_D^{25} - 34.4^\circ$  in EtOH, converted by Ac<sub>2</sub>O in C<sub>5</sub>H<sub>5</sub>N at room temp. into the 3( $\beta$ )-acetate, m.p. 165.5—166.5°,  $[\alpha]_D^{25} - 41.6^\circ$  in CHCl<sub>3</sub>, which is hydrogenated (PtO<sub>2</sub> in AcOH at 50°) to 3( $\beta$ )-acetoxynorallocholenyldimethylcarbinol, m.p. 161—162°,  $[\alpha]_D^{25} + 5.6^\circ$  in CHCl<sub>3</sub>; this is oxidised (CrO<sub>3</sub> in AcOH) and then esterified (CH<sub>2</sub>N<sub>2</sub>) to (I). (III) is converted by an excess of MgPhBr into  $\Delta^{5:6-23:24}$ -3( $\beta$ )-acetoxysuccinyl-24:24-diphenylcholadiene, m.p. 172—173°, converted by successive treatments with Br in CCl<sub>4</sub>, CrO<sub>3</sub> in AcOH, Zn dust, and AcOH, CH<sub>2</sub>N<sub>2</sub>, and Ac<sub>2</sub>O-C<sub>5</sub>H<sub>5</sub>N into Me  $\Delta^{5:6}$ -3( $\beta$ )-acetoxynorcholenate, m.p. 133.5—135.5°,  $[\alpha]_D^{25} - 45.7^\circ$  in CHCl<sub>3</sub>, which is hydrolysed to (II). M.p. are corr. (vac.). H. W.

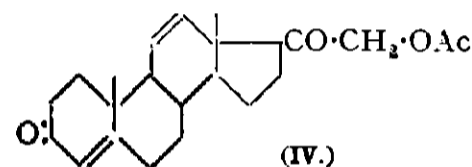
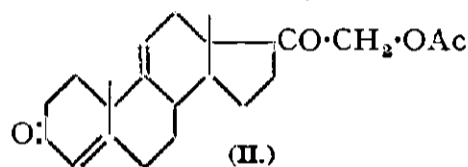
**Structure of choleic acids.** N. P. Buu-Hoi (*Z. physiol. Chem.*, 1943, 278, 230—235).—Deoxycholic acid (I) forms 8:1 compounds with chaulmoogric, m.p. 185—186°, hydnocarpic, m.p. 183°, dihydrochaulmoogric, m.p. 186°, and dihydrohydnocarpic acid, m.p. 182—183°, Et chaulmoograte, m.p. 187°, hydnocarpate, m.p. 186—187°, dihydrochaulmoograte, m.p. 188°, and dihydrohydnocarpate, m.p. 185—186°, chaulmoogryl, m.p. 185—186°, and dihydrochaulmoogryl alcohol, m.p. 186—187°, and Et  $\kappa$ -phenylundecate, m.p. 174°. (I) forms 4:1 compounds with CH<sub>2</sub>Ph·CO<sub>2</sub>Me, m.p. 168—169° (after sintering), and BuOBz, m.p. 169—170° (after sintering), and 6:1 compounds with Ph·[CH<sub>2</sub>]<sub>3</sub>·CO<sub>2</sub>Et, m.p. 170—172° (after sintering), and 1-C<sub>10</sub>H<sub>7</sub>·CH<sub>2</sub>·CN, m.p. 175—177° (after sintering). Hence the theory of Kratky *et al.* (cf. A., 1937, I, 118) requires modification. W. McC.

**Androstanolones substituted in the 17-position.**—See B., 1943, III, 279.

**Steroids and sex hormones. LXXXV. D-Homoandrostane derivatives, a group of highly active androgens.** M. W. Goldberg and E. Wydler (*Helv. Chim. Acta*, 1943, 26, 1142—1155; cf. A., 1943, II, 199).—*trans*-Dehydroandrosterone 3-monoacetate is converted by KCN and AcOH in EtOH at  $>0^\circ$  into its cyanohydrin, hydrogenated (PtO<sub>2</sub> in AcOH) to 17-hydroxy-3( $\beta$ )-acetoxyl-17-aminomethylandrosterane, m.p. 234—236°, which is converted by HNO<sub>2</sub> into (mainly) 17a-keto-(I), m.p. 120—122°, and 17-keto-3( $\beta$ )-acetoxyl-D-homoandrostane (II), m.p. 102—104°,  $[\alpha]_D^{25} - 3.7^\circ$  in dioxan [semicarbazone, m.p. 251—253° (decomp.)]. (II) is hydrolysed to 3( $\beta$ )-hydroxy-17-keto-D-homoandrostane, m.p. 170—172°,  $[\alpha]_D^{25} + 23^\circ$  in dioxan, oxidation (CrO<sub>3</sub>, AcOH) of which affords 3:17-diketo-D-homoandrostane, m.p. 168—170°,  $[\alpha]_D^{25} - 32^\circ$  in dioxan. The isomeric 3:17a-diketone, m.p. 183—185°,  $[\alpha]_D^{25} - 27^\circ$  in dioxan, is obtained by hydrolysing and oxidising (I). Both diketones are converted by successive treatments with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O and NaOEt into D-homoandrostane, m.p. 85.87°,  $[\alpha]_D^{25} - 3.7^\circ$  in dioxan. Hydrogenation (PtO<sub>2</sub> in AcOH) followed by benzylation of (I) and chromatography of the product leads to D-homoandrostane-3( $\beta$ ):17a( $\alpha$ )-diol 3-acetate 17-benzoate, m.p. 201—202°,  $[\alpha]_D^{25} + 17.6^\circ$  in dioxan (cf. A., 1940, II, 350), and -3( $\beta$ ):17a( $\beta$ )-diol 3-acetate 17-benzoate, m.p. 139—142°,  $[\alpha]_D^{25} - 10.7^\circ$  in dioxan. These are partly hydrolysed (KHCO<sub>3</sub> in boiling aq. MeOH) to the respective benzoates, m.p. 230—233°,  $[\alpha]_D^{25} - 59^\circ$  in dioxan, and m.p. 154—155°,  $[\alpha]_D^{25} - 50.7^\circ$  in dioxan. Complete hydrolysis gives 3( $\beta$ ):17a( $\alpha$ )-, m.p. 217—218°  $[\alpha]_D^{25} + 26^\circ$  in dioxan, and 3( $\beta$ ):17a( $\beta$ )-dihydroxy-D-homoandrostane, m.p. 219—220°,  $[\alpha]_D^{25} - 16^\circ$  in dioxan. Oxidation of the respective alcohols yields 3-keto-17a( $\beta$ )-, m.p. 132—133°,  $[\alpha]_D^{25} - 35.5^\circ$  in dioxan, and 3-keto-17a( $\alpha$ )-benzoyloxyandrosterane, m.p. 194—195°,  $[\alpha]_D^{25} + 28^\circ$  in dioxan (D-homodihydrotestosterone 17a( $\beta$ )- and 17a( $\alpha$ )-benzoates). 3-Keto-

17a( $\alpha$ )-acetoxyl-D-homoandrostane (D-homodihydrotestosterone 17a( $\alpha$ )-acetate), m.p. 194—195°,  $[\alpha]_D^{25} + 9.8^\circ$  in dioxan, obtained by acetylation of the OH-compound (*loc. cit.*), is converted by Br in AcOH containing conc. aq. HBr into the 2-Br-derivative, m.p. 214—215°,  $[\alpha]_D^{25} + 21^\circ$  in dioxan; this affords a pyridinium compound, m.p. 280° (decomp.), which passes when heated into (?)  $\Delta^4$ -3-keto-17a( $\alpha$ )-acetoxyl-D-homoandrostane, m.p. 158.5—160°,  $[\alpha]_D^{25} + 80.3^\circ$  in dioxan. The derivatives of the D-homoandrostane series appear as active physiologically as the corresponding compounds of the natural steroid series. M.p. are corr. H. W.

**Constituents of the adrenal cortex and related substances. LXIII. 11-epiCorticosterone acetate and two isomeric anhydrocorticosterone acetates.** C. W. Shoppee and T. Reichstein (*Helv. Chim. Acta*, 1943, 26, 1316—1328; cf. A., 1940, II, 350; 1941, II, 259).—Corticosterone acetate (I), m.p. 147.5—148.5°,  $[\alpha]_D^{25} + 195^\circ \pm 3^\circ$ ,  $[\alpha]_{5461}^{20} + 236^\circ \pm 3^\circ$  in CMe<sub>2</sub>, is converted by boiling conc. HCl-AcOH (1:9) (30 min.) into (after reacylation) anhydrocorticosterone acetate (II), m.p. 159—160°,  $[\alpha]_D^{25} + 129^\circ \pm 2^\circ$ ,  $[\alpha]_{5461}^{20} + 150^\circ \pm 2^\circ$  in CMe<sub>2</sub> (yield 35—40%), and 11-epicorticosterone acetate (III), m.p. 122—125°,  $[\alpha]_D^{25} + 187^\circ \pm 4^\circ$ ,  $[\alpha]_{5461}^{20} + 222^\circ \pm 4^\circ$  in CMe<sub>2</sub>. (III) does not give a colour with C(NO<sub>2</sub>)<sub>4</sub>, rapidly reduces Ag<sub>2</sub>O-NH<sub>3</sub>, and gives a green fluorescence in conc. H<sub>2</sub>SO<sub>4</sub>. Dehydration of (I) under more energetic conditions (conc. HCl-AcOH, 1:4) gives unchanged material, no (III), (II) (26%), an anhydrocorticosterone acetate (IV) (17%), m.p. 142—143°,  $[\alpha]_D^{25} + 98^\circ \pm 6^\circ$ ,  $[\alpha]_{5461}^{20} + 130^\circ \pm 6^\circ$  in CMe<sub>2</sub>, and a very small amount of a substance, m.p. 169°. (II) is largely unchanged when boiled for 30 min. with conc. HCl-AcOH (1:9), but is partly converted into (IV) by the boiling 1:4 mixture, which partly transforms (III) into (II) and (IV). (III) is oxidised (CrO<sub>3</sub> in AcOH) to dehydrocorticosterone acetate, m.p. 178—181.5°,  $[\alpha]_D^{25}$



$+215^\circ \pm 8^\circ$ ,  $[\alpha]_{5461}^{20} + 266^\circ \pm 8^\circ$  in CMe<sub>2</sub>. In the Everse-de Fremery test (II) is 2—3 times more powerful than deoxycorticosterone acetate (V) and is about equally or somewhat less active towards adrenalectomised rats. In the former test (IV) is 2—3 times less active than (V). M.p. are corr. H. W.

## V.—TERPENES AND TRITERPENOID SAPOGENINS.

**cis- $\Delta^2$ -Menthene.** W. Hüchel and H. Wagner (*Ber.*, 1941, 74, [B], 657—662).—Catalytic reduction of *l*-piperitone (I),  $[\alpha]_D^{25} - 50.6^\circ$ , is reinvestigated (cf. A., 1939, II, 434). It is established that (I) contains some racemate and that *d*-menthone is produced as well as *d*-isomenthone. Vals. of  $[\alpha]$  (for different  $\lambda$  and various solvents) are given for *d*-neoisomenthol (phenylcarbamate, m.p. 91—92°,  $[\alpha]_D^{25} - 12.4^\circ$  in EtOH; H phthalate, m.p.  $\sim 85$ —86°,  $[\alpha]_D^{25} - 18.0^\circ$  in CHCl<sub>3</sub>). *dl*-isoMenthyl H phthalate has m.p. 116—117° (lit. 107—108°). *d*-isoMenthyl *p*-toluenesulphonate (*loc. cit.*) with boiling EtOH-NaOEt gives 60% of *cis*- $\Delta^2$ -menthene (II), b.p. 46—48°/10 mm.,  $[\alpha]_D^{25} + 45.2^\circ$ ; differences in physical data for (II) and *trans*- $\Delta^2$ -menthene are in accordance with the Auwers-Skita rule. Treatment of (II) with *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>H in EtOH causes a slight reduction in  $\alpha_D$ ; if this is not due to racemisation then (II) contains some  $\Delta^3$ -menthene (III). *d*-isoMenthylamine and HNO<sub>2</sub> give *d*-isomenthol and a mixture of (II) (50%), *r*-(III) (38%), and active (III) (12%). H. B.

**1:5-meso-Methylenecycloheptane, the dicyclic ring homologue of norcamphane.** J. von Braun and J. Reitz (*Ber.*, 1941, 74, [B], 273—275; cf. A., 1937, II, 404).—Homonorcamphancarboxylic acid in conc. H<sub>2</sub>SO<sub>4</sub> with HN<sub>3</sub> in CHCl<sub>3</sub> affords 60% of 2-amino-1:5-meso(=endo)methylenecycloheptane (I), b.p. 69—70°/14 mm. (platinichloride, m.p. 275—280°; picrate, m.p. 180°; Bz derivative, m.p.  $\sim 95^\circ$ ). (I) is treated with Me<sub>2</sub>SO<sub>4</sub> etc.; the methoxide with KOH yields 38% of 2-dimethylamino-1:5-meso-methylenecycloheptane, b.p. 83°/13 mm. (platinichloride, m.p. 173°; picrate, m.p. 197°), and 45% of 1:5-meso-methylene- $\Delta^2$ -cycloheptene, b.p. 132°, which when hydrogenated over Pd gives 1:5-meso-methylenecycloheptane, b.p. 131°. J. WA.

**Nitrobornylphenols.**—See B., 1943, III, 239.

**Position of substituents in Reychler's sulphocamphoric acid and the so-called  $\beta$ -bromocamphor.** G. Komppa (*J. pr. Chem.*, 1943, [ii], 162, 19—28).—The  $\omega$ -position of the Br in " $\beta$ "-bromocamphor (I) and " $\beta$ "-bromocamphoric acid (II) is substantiated. For steric reasons *dl*-(I), m.p. 78°, does not react with Mg or moist Ag<sub>2</sub>O. The camphor skeleton of *dl*-(II), m.p. 207—208° (decomp.) (anhydride, m.p. 148—149°), is confirmed by reduction by Zn dust in AcOH to *dl*-camphoric acid (anhydride, m.p. 229°). In boiling 20% aq. KOH (Cu vessel), (II) gives *dl*- $\omega$ -hydroxycamphoric acid (III) (80%), m.p. 158—159°, converted by AcCl into the  $\omega$ -acetate anhydride, m.p. 123—124°, and thence the  $\omega$ -acetate toluididic acid, m.p. 124°. With dil. HNO<sub>3</sub>, (III) gives indefinite products, but

with 1%  $\text{KMnO}_4$  at 60–70° gives a good yield of *carboxyapocamphoric acid*, m.p. 195–196°, which at > the m.p. yields (mainly *cis*-) *apocamphoric acid*, identified also as anhydride and anilide. The  $\text{Me}_2$  ester (prep. by  $\text{MeOH-H}_2\text{SO}_4$  or by way of the chloride), m.p. 137°, in boiling  $\text{NPhEt}_3$  gives  $\text{MeBr}$ ,  $\text{CO}_2$ , and *Me dl-a-campholytate* (IV) (~54%), b.p. 67–70°/8 mm., and thence by dil.  $\text{HCl}$  *dl-β-campholytic (dl-isolauronic) acid* (V), m.p. 132–133° (dibromide, m.p. 138–139°). The  $\text{Et}_2$  ester, m.p. 102–103°, of (II) gives similarly the *Et* ester corresponding to (IV). With  $\text{Ag}_2\text{O}$  in aq.  $\text{EtOH}$  at 30°, (II) gives the stable lactone, *dl-ω-camphanic acid* (65%), m.p. 151–152°, which, when heated, gives (V) and  $\text{CO}_2$ . The true  $\beta$ -bromo- and  $\beta$ -hydroxy-camphoric acid of Toivonen (*Ann. Acad. Sci. Fennicae*, 1927, A, 29, No. 10) differ from (I) and (II) in m.p. R. S. C.

**Effect of phenyl group on rotatory power: phenylcamphoranilic acids and *p*-diphenylylimino-*d*-camphor.** M. Singh and A. Singh (*Indian Chem. Soc.*, 1942, 19, 145–148).—In comparison with that of other substituted camphoranilic acids,  $[\alpha]_D^{20}$  in  $\text{MeOH}$  of 4', m.p. 196–197° (shrinks at 194°), is abnormally high (+64°), that of 3', m.p. 204–205°, abnormally low (+40.8°), and that of 2'-phenylcamphoranilic acid, m.p. 181° [from camphoric anhydride,  $\text{C}_6\text{H}_4\text{Ph-NH}_2$ , and  $\text{NaOAc}$  at 130–135° (120° for the *o*- and *m*-compounds)], normal (+26.5°). In each case  $[\alpha]_D$  of the Na salt is > of the free acid in org. solvents. *p*-Diphenylylimino-*d*-camphor (from camphorquinone,  $p\text{-C}_6\text{H}_4\text{Ph-NH}_2$ , and anhyd.  $\text{Na}_2\text{SO}_4$  at 100°), m.p. 148–149°,  $[\alpha]_D^{20}$  +696.8° in  $\text{MeOH}$ , +720.7° in  $\text{EtOH}$  (anilino-camphor has  $[\alpha]_D^{20}$  +606.8° in  $\text{MeOH}$ ), is reduced ( $\text{Zn} + 10\% \text{ KOH}$ ) to *p*-diphenylaminocamphor,  $[\alpha]_D^{20}$  +82.3° in  $\text{EtOH}$ . A. Li.

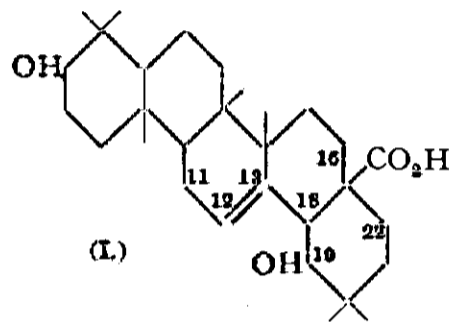
**Sesquiterpenes. LX. Oxidative degradation of norcedrenedicarboxylic acid by nitric acid.** P. A. Plattner and H. Kläui (*Helv. Chim. Acta*, 1943, 26, 1553–1559; cf. A., 1943, II, 97).—Cedrene (I) is brominated by  $(\text{CH}_2\text{CO})_2\text{NBr}$  in boiling  $\text{CCl}_4$  and the crude bromocedrene (which cannot be distilled in a vac. without decomp.) is oxidised by  $\text{KMnO}_4$  in boiling aq.  $\text{COMe}_2$  followed by boiling aq.  $\text{HNO}_3$  to norcedrenedicarboxylic acid (II). The mother-liquors from (II) contain  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  and  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (III). This has been obtained previously by the oxidation of cedrene and temporarily regarded as camphoronic acid (cf. Plattner, *et al.*, A., 1943, II, 97; Treibs, *Ber.*, 1943, 76, 160). Contrary to Treibs, (III), m.p. 145–145.5°,  $[\alpha]_D$  –8° in  $\text{H}_2\text{O}$ , is best obtained by the protracted oxidation of (I) with  $\text{HNO}_3$  ( $d$  1.4) at 100–115°. Elimination of  $\text{HBr}$  from bromonorcedrenedicarboxylic ester carried out in an autoclave instead of a sealed tube gave relatively little dehydronorcedrenedicarboxylic acid and much oily mother-liquor which, when oxidised with  $\text{KMnO}_4$  in alkaline solution, yields *trans-norcedrenedicarboxylic acid*, m.p. 222.5–223°,  $[\alpha]_D^{25}$  –53.3° in  $\text{CHCl}_3$ , converted by boiling  $\text{Ac}_2\text{O}$  into the norcedrenedicarboxylic anhydride, m.p. 126–127°. M.p. are corr. H. W.

**Constitution of cafestol.** V. A. Wettstein, F. Hunziker, and K. Miescher (*Helv. Chim. Acta*, 1943, 26, 1197–1218; cf. A., 1943, II, 199, 203).—Ozonisation of epoxynorcafestadienone (I) in  $n\text{-C}_8\text{H}_{14}$  or  $\text{CCl}_4$  and treatment of the ozonide with boiling  $\text{H}_2\text{O}$  gives as main product a difficultly volatile, non-cryst. acid (II) transformed by esterification ( $\text{CH}_2\text{N}_2$ ), chromatographic purification, and alkaline hydrolysis into the *Me H* ester (III),  $\text{C}_{18}\text{H}_{26}\text{O}_5$ , m.p. 156–157°,  $[\alpha]_D^{18}$  +25.7° ± 2° in dioxan. (III) is transformed by  $\text{CH}_2\text{N}_2$  into the  $\text{Me}_2$  ester, m.p. 53–55°, which gives a *monosemicarbazone*, m.p. 211–213° (decomp.). Although (III) cannot be hydrolysed, its  $\text{OMe}$  is not present in (II), which does not contain  $\text{OAlk}$  (Zeisel) and is transformed by  $\text{EtOH}$  and mineral acid into the  $\text{Et}_2$  ester,  $\text{C}_{21}\text{H}_{32}\text{O}_5$ , m.p. 104–105°, hydrolysed to the *Et H* ester (IV), m.p. 162–163°. (III) is converted by  $\text{EtOH}$ –mineral acid into the *Me Et* ester, m.p. 86–88°, and (IV) affords analogously an isomeric *Me Et* ester, m.p. 126–128°. In all probability (II) is therefore  $\text{C}_{17}\text{H}_{24}\text{O}_5$  and contains only 3 intact C rings. The formation of (II) is accompanied by the elimination of 2 C but not of H and involves the loss of etheral O and formation of  $\text{CO}_2$ . The furan ring and a C ring are opened. It appears therefore the  $\text{C}_{(2)}$  and  $\text{C}_{(3)}$  of the furan ring in cafestol (V) are attached to H whereas  $\text{C}_{(4)}$  and  $\text{C}_{(5)}$  participate in the formation of an *ortho*-condensed C ring. A strict proof that the furan ring of (V) is substituted at  $\text{C}_{(4)}$  and  $\text{C}_{(5)}$  and only in these positions is afforded by the observation that the adduct from cafestyl acetate (VI) and  $(\text{CH}\cdot\text{CO})_2\text{O}$  is converted by successive treatments with  $\text{HCl}$ – $\text{AcOH}$  at 90°, 33%  $\text{HNO}_3$  at 190–200°, and  $\text{CH}_2\text{N}_2$  into 1:2:3:4- $\text{C}_6\text{H}_2(\text{CO}_2\text{Me})_4$ . Since a H has been shown previously to be attached to  $\text{C}_{(2)}$ , this must be true also of  $\text{C}_{(3)}$  and the furan ring of (V) must be attached to the remainder of the mol. by  $\text{C}_{(4)}$  and  $\text{C}_{(5)}$ . (I) is converted by  $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  in  $\text{Et}_2\text{O}$  at 0° into a non-cryst. product, transformed ( $\text{Ac}_2\text{O}$ – $\text{C}_5\text{H}_5\text{N}$  at room temp.) directly or after treatment by  $\text{HClO}_4$  into a *ketoacetoxynorcafestenolide*,  $\text{C}_{21}\text{H}_{26}\text{O}_5$ , m.p. 239–240°. The requirement of 2 equivs. of alkali for hydrolysis, the presence of 1 Ac and absence of active H, together with the formation of a *monosemicarbazone*, m.p. 278° (decomp.), show the 5 O to be present in keto, Ac, and lactone groups. According to the absorption spectrum, a double linking

is in the  $\alpha\beta$  position to the lactone group. The substance does not decolorise  $\text{Br-AcOH}$  or  $\text{KMnO}_4\text{-EtOH}$ , does not give the Legal or Baljet reactions, and does not reduce  $\text{Ag}_2\text{O-NH}_3$ . It is stable towards  $\text{O}_3$  and  $\text{CrO}_3\text{-AcOH}$  at low temp. Its alkaline hydrolysis leads to a compound,  $\text{C}_{19}\text{H}_{24}\text{O}_4$ , m.p. 257–261° (decomp.), which does not give a quinoxaline derivative. It probably has the partial

structure  $\begin{array}{c} \text{CH}\cdot\text{CO} \\ | \\ \text{C}-\text{C}(\text{OAc}) \end{array} \text{O}$ . Analogously (VI) is oxidised by  $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  and then acetylated to a *hydroxydiacetoxycafestenolide*,  $\text{C}_{24}\text{H}_{32}\text{O}_7$ , m.p. 197–198°. Crude (II) is transformed by  $\text{Ac}_2\text{O}$  followed by distillation in vac. into a *diketone* (VII),  $\text{C}_{18}\text{H}_{22}\text{O}_2$ , m.p. 204–205°, characterised by a *disemicarbazone*, m.p. >400°, darkens >300°, showing according to Blanc's rule that the original ring A is 6- or 7-membered. Analogously the  $\text{Me}_2$  or  $\text{Me Et}$  ester of (II) is cyclised by Na in boiling  $\text{PhMe}$  to a  $\beta$ -ketocarboxylic ester ketone, converted by boiling conc.  $\text{HCl-EtOH}$  into (VII). The ready formation of a *m-nitrobenzylidene* derivative, m.p. 227–229°, of (VII) is ascribed to the at. grouping in the contracted ring A since cafestol derivatives which contain CO or  $\text{CH}_2$  exclusively in ring D do not react with  $\text{ArCHO}$ .  $\text{C}_{(5)}$  or  $\text{C}_{(6)}$  must be present in  $\text{CH}_2$  and also the neighbouring  $\text{C}_{(6)}$  or  $\text{C}_{(7)}$  must be united to at least 1 H atom. 17 of the 20 C atoms of cafestol are thus accounted for and the nature and mode of union of all substituents and double linkings is explained. *Piperonylidenenorcafestanediene* has m.p. 164–165°. M.p. are corr. H. W.

**Triterpenes. LXXVII. Siarsinolic acid.** L. Ruzicka, A. Grob, R. Egli, and O. Jeger (*Helv. Chim. Acta*, 1943, 26, 1218–1235).—Evidence is adduced in favour of the view that siarsinolic acid (I)



is  $\Delta^{12:13-2}$ :19-dihydroxy-28-oleanenic acid. (I), m.p. 279–280°,  $[\alpha]_D$  +39.2° in abs.  $\text{EtOH}$  (prep. from Siamese gum benzoin described), is converted into its *Me* ester (II), m.p. 182°,  $[\alpha]_D$  +44.9°, by  $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O}$  (also obtained from the K salt and  $\text{Me}_2\text{SO}_4$  in somewhat alkaline  $\text{MeOH}$ ); the *Et* ester, m.p. 175–176°,  $[\alpha]_D$  +44.6° in  $\text{EtOH}$ , is prepared from  $\text{EtI}$  and the Ag salt in boiling abs.  $\text{Et}_2\text{O}$ . (I) and  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  at room temp. afford 2-acetylsiarsinolic acid [ $\Delta^{12:13-19}$ -hydroxy-2-acetoxy-28-oleanenic acid], m.p. 282–284°,  $[\alpha]_D$  +48.7°, converted by  $\text{CH}_2\text{N}_2$  into the *Me* ester (III), m.p. 125–127° (lit. 110–120°),  $[\alpha]_D$  +47.5°, also obtained by acetylation of (II) and hydrolysed to (II) by boiling  $\text{KOH-MeOH}$ . Passage of dry  $\text{HCl}$  through (III) in  $\text{Ac}_2\text{O}$  at 100° leads to *Me isodiacylsiarsinolate*, (IV), m.p. 234–236°,  $[\alpha]_D$  +41.3°, also obtained from the corresponding acid, m.p. 262°,  $[\alpha]_D$  +40°, and  $\text{CH}_2\text{N}_2$ . It is hydrolysed by boiling  $\text{N-KOH}$  to *Me iso-19-acetylsiarsinolate* (V), m.p. 235–237°,  $[\alpha]_D$  +40.7°, converted by  $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$  at room temp. into (IV) and by Claisen's reagent at 150° into (I). Analogously the acid is converted by mild hydrolysis into iso-19-acetylsiarsinolic acid, m.p. 235–237°,  $[\alpha]_D$  +39°, and by vigorous hydrolysis into (I). (III) and dry  $\text{HCl}$  in  $\text{Ac}_2\text{O}$  at room temp. afford *Me iso-2-acetylsiarsinolate* (VI), m.p. 237–238°,  $[\alpha]_D$  +48.5°, also obtained similarly from (II) and acetylated ( $\text{Ac}_2\text{O-HCl}$  at 100°) to (IV). It is gently hydrolysed to *Me isosiarsinolate*, m.p. 205–206°, re-acetylated ( $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$  at room temp.) to (V) and energetically hydrolysed to (II). iso-2-Acetylsiarsinolic acid, m.p. 273–274° (much decomp.),  $[\alpha]_D$  +40°, is hydrolysed by boiling  $\text{N-KOH-MeOH}$  to (I). (V) is oxidised by  $\text{CrO}_3$  ( $\equiv 1.5 \text{ O}$ ) in  $\text{AcOH}$  at room temp. to *Me iso-2-keto-19-acetoxy-28-oleanenoate*, m.p. 225–227°,  $[\alpha]_D$  +50.4° ( $c = 1.43$ ) and +48° ( $c = 2.29$ ), which is not hydrolysed by boiling 2N-KOH in 2 days. Similarly (III) affords *Me 19-keto-2-acetoxy-28-oleanenoate*, m.p. 244–247°,  $[\alpha]_D$  +107.6° ( $c = 1.56$ ) and +110° ( $c = 3.36$ ), which gives a marked yellow colour with  $\text{C}(\text{NO}_2)_4$  and does not appear to yield a semicarbazone; it is hydrolysed by boiling  $\text{N-KOH-MeOH}$  or boiling conc.  $\text{HCl-MeOH}$  to *Me*  $\Delta^{13:18}$ -19-keto-2-hydroxy-28-oleanenoate (VII), m.p. 209–210° (lit. 189–190°),  $[\alpha]_D$  –209.0°. It is also obtained from *Me*  $\Delta^{12:13-19}$ -keto-2-acetoxyoleanenoate and  $\text{HCl}$  in  $\text{AcOH}$  at room temp. (VI) is oxidised to *Me iso-19-keto-2-acetoxy-28-oleanenoate*, m.p. 221–223°,  $[\alpha]_D$  +62.2°, hydrolysed to the 2-OH-ester, m.p. 195–197°  $[\alpha]_D$  +46.0°, from which it is re-formed by  $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$  at room temp. Addition of  $\text{CrO}_3$  to a solution of (I) in  $\text{AcOH}$  containing conc.  $\text{H}_2\text{SO}_4$  at room temp. gives a non-homogeneous product from which *Me*  $\Delta^{12:13-2}$ :19-diketo-28-oleanenoate, m.p. 211–212° (lit. 207–208°),  $[\alpha]_D$  +139.8° ( $c = 0.361$ ), +140.5° ( $c = 0.642$ ) (oxime, m.p. 232–233°; semicarbazone, m.p. 233–234°), is isolated. It is also obtained from (II). It is not affected by  $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$  at room temp. or catalytically hydrogenated in  $\text{AcOH}$  containing  $\text{PtO}_2$ . Oxidation ( $\text{CrO}_3$  in  $\text{AcOH}$  at room temp.) of (VII) affords *Me*  $\Delta^{13:18-2}$ :19-diketo-28-oleanenoate, m.p. 193–194°,  $[\alpha]_D$  –189.0° [semicarbazone, m.p. 250–251° (decomp.)], which does not give a yellow colour with  $\text{C}(\text{NO}_2)_4$ . The semicarbazone of *Me*  $\Delta^{12:13-2}$ -keto-19-hydroxy-28-oleanenoate is transformed by  $\text{NaOEt}$  in  $\text{EtOH}$  at 180° into *Me*  $\Delta^{12:13-19}$ -hydroxy-28-oleanenoate, m.p. 213–214°, which is un-

changed by  $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ ; it is oxidised to *Me*  $\Delta^{12:13}$ -19-*keto*-28-*oleanenoate*, m.p. 204—205°. M.p. are corr.  $[\alpha]_D$  are in  $\text{CHCl}_3$  unless otherwise stated. H. W.

**Triterpenes. LXXVIII. Introduction of additional double linkings into the  $\alpha$ - and  $\beta$ -amyrin types with *N*-bromosuccinimide.** L. Ruzicka, O. Jeger, and J. Redel [with, in part, W. Hofer] (*Helv. Chim. Acta*, 1943, **26**, 1235—1240).— $\beta$ -Amyrin acetate and  $(\text{CH}_2\text{CO})_2\text{NBr}$  in  $\text{CCl}_4$  at 100° afford  $\beta$ -*amyratrienyl acetate* (I), m.p. 185°,  $[\alpha]_D + 527$  in  $\text{CHCl}_3$ , which gives a marked brown colour with  $\text{C}(\text{NO}_2)_4$ . It is hydrolysed by alkali to  $\beta$ -*amyratrienol*, m.p. 179—180°, re-acetylated ( $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$  at room temp.) to (I).  $\alpha$ -Amyrin acetate and  $(\text{CH}_2\text{CO})_2\text{NBr}$  in boiling  $\text{CCl}_4$  afford  $\alpha$ -*amyradienyl acetate* (II), m.p. 166—167°,  $[\alpha]_D + 334$  in  $\text{CHCl}_3$ . Similarly *Me* acetylursolate yields *Me* *acetyldehydroursolate*, m.p. 229—230°,  $[\alpha]_D + 254$  in  $\text{CHCl}_3$ , hydrolysed ( $\text{KOH}-\text{EtOH}$  at 170°) to *dehydroursolic acid*, m.p. 277—279° (decomp.),  $[\alpha]_D + 291$  in  $\text{C}_5\text{H}_5\text{N}$  [acetate, m.p. 287—288° (decomp.),  $[\alpha]_D + 272$  in  $\text{C}_5\text{H}_5\text{N}$ ]. An amended method for the prep. of (II) from  $\alpha$ -amyrin benzoate and S in  $\text{CH}_2\text{Ph}\cdot\text{OAc}$  under  $\text{N}_2$  at 220° is described. M.p. are corr. H. W.

**Triterpenes. LXXIX. Relationships between  $\alpha$ -elemolic acid and the so-called " $\beta$ -elemenic acid."** L. Ruzicka, E. Rey, M. Spillmann, and H. Baumgartner (*Helv. Chim. Acta*, 1943, **26**, 1638—1658).—Chemical and physical evidence shows that " $\beta$ -elemenic acid" (I) is directly related to  $\alpha$ -elemolic acid (II) in position of the double linking and hence should be termed  $\alpha$ -elemenic acid (III). To avoid confusion it is proposed to discontinue the use of  $\alpha$ - and  $\beta$ - in this series and to adopt a rational nomenclature for the elemic acid group based on the name "elemene" for the unknown, saturated parent hydrocarbon. The old and new (in parentheses) nomenclature is as follows: (II) (elemadienolic); dihydro- $\alpha$ -elemolic (IV) (elemenic);  $\beta$ -elemolic (V) (*epielemadienolic*); dihydro- $\beta$ -elemolic (VI) (*epielemenic*); *epi*- $\alpha$ -elemolic (*epi*-*isoelemadienolic*); *epi*dihydro- $\alpha$ -elemolic (*epi*-*isoelemenic*); isomeric (II), from (IV) +  $\text{SeO}_2$  (dehydroelemenic or isomeric elemadienolic acid); (III) (*isoelemadienonic*); dihydro- $\alpha$ -elemenic (VII) (*isoelemenic*); (I) (elemadienonic); dihydro- $\beta$ -elemenic (VIII) (elemenic); deoxo- $\alpha$ -elemenic (*isoelemadienic*); dihydrodeoxo- $\alpha$ -elemenic (*isoelemenic*); deoxo- $\beta$ -elemenic (elemadienic); dihydrodeoxo- $\beta$ -elemenic (elemenic); diketodihydro-2- $\alpha$ -elemolic (IX) (*isoelemadienonic*); diketodihydro- $\beta$ -elemolic (*epi*-*isoelemadienonic*); dihydro- $\beta$ -elemolaldehyde (*epielemenal*); dihydro- $\beta$ -tritelemonol (*epielemenal*);  $\beta$ -tritelemonol (*epielemadienediol*); trisnor- $\alpha$ -tritelemonoldicarboxylic (trisorolemonoldicarboxylic); trisnor- $\alpha$ -tritelemononedicarboxylic (*isotrisorolemononedicarboxylic*); trisnor- $\beta$ -tritelemononedicarboxylic (trisorolemononedicarboxylic) acid. The following general survey of experimental results in the series is given. Hydrogenation of the  $>\text{CO}$  group with Na and EtOH leads invariably to the isolation of *epi*-compounds since in this reaction the isomerides with normal position of OH are formed in very small amount. Catalytic and Meerwein and Ponndorf's methods yield compounds with normal and *epi* OH groups together in isolable amount although members of each series have not actually been isolated previously in all operations, since the separations have not been carried sufficiently far. Oxidation with  $\text{CrO}_3$  or according to Oppenauer gives  $>\text{CO}$  compounds with unchanged position of the double linkings and those with conjugated double linkings (*iso*-series). Dehydrogenation with Cu at 300° gives exclusively  $>\text{CO}$  compounds with unchanged position of the double linkings. The following transitions are recorded: (IV) is oxidised by  $\text{CrO}_3$  in aq. AcOH at 50° to (VII), m.p. 309—310°,  $[\alpha]_D - 97.0$  [*Me* ester, m.p. 152—153°,  $[\alpha]_D - 95.3$ ; oxime, m.p. 233—234° (decomp.),  $[\alpha]_D - 117.2$ ], and (VIII), m.p. 251—252 [oxime, m.p. 235—237° (decomp.)]. (IV) is dehydrogenated by Cu powder at 270—300° to (VIII), m.p. 224—225° [oxime, m.p. 219—220° (decomp.)], reduced ( $\text{PtO}_2$  in AcOH at room temp.) to (VI), m.p. 251—252°,  $[\alpha]_D + 14.9$ , and by Na and EtOH to (V), m.p. 232—233°,  $[\alpha]_D + 9.6$ . (V) is dehydrogenated by Cu powder to (VIII). (IV) is converted by  $\text{NaOEt}-\text{EtOH}$  at 180—190° followed by  $\text{CH}_2\text{N}_2$  into *Me* elemadienolate (X), m.p. 149—150°,  $[\alpha]_D - 11.7$ ; treatment of the non-cryst. residue with  $\text{H}_2$  ( $\text{PtO}_2$  in AcOH) followed by acetylation gives *Me* *epiacetyl*elemenolate, m.p. 136.5—137°,  $[\alpha]_D + 15.35$ . *Me* elemadienolate (XI) is reduced [ $\text{Al}(\text{OPr})_3$  in  $\text{Pr}^2\text{OH}$ ] to *Me* elemadienolate, m.p. 149.5—150°,  $[\alpha]_D - 13.8$  (acetate, m.p. 114—115°,  $[\alpha]_D - 40.8$ ); the non-cryst. residue is hydrogenated and acetylated to *Me* *epiacetyl*elemenolate, m.p. 137—137.5°,  $[\alpha]_D + 12.5$ . Oxidation (Oppenauer) of (X) gives a mixture of approx. equal amounts of (XI) and *Me* *isoelemadienolate*. The alkaline hydrolysis of acetyl- and *epiacetyl*-elemadienolic acid has been followed quantitatively. Reduction of (VII) by Na and EtOH and acetylation of the product leads to *epi*-*iso*acetyl $\alpha$ -elemenic acid, m.p. 253—254°, oxidised ( $\text{CrO}_3$  in AcOH at 100°) to *epi*-*iso*acetyl $\alpha$ -elemenic acid (XII), m.p. 271—272°,  $[\alpha]_D + 22.6$ .  $\text{CrO}_3$  in AcOH at 100° oxidises (VII) to *isoelementronic acid* (XIII), m.p. 291—292°,  $[\alpha]_D + 6.8$  also obtained similarly from (IX) and (V). (XII) is hydrolysed (boiling  $\text{KOH}-\text{MeOH}$ ) to *epi*-*isoelemendionolic acid*, m.p. 275—276°,  $[\alpha]_D + 3.8$ , oxidised ( $\text{CrO}_3$  in AcOH at room temp.) to (XIII). *iso*Acetyl $\alpha$ -elemendionolic acid similarly affords (IX), m.p. 269—270°,  $[\alpha]_D$

—11.4°, oxidised to (XIII). M.p. are corr. (vac.).  $[\alpha]_D$  are in  $\text{CHCl}_3$ . H. W.

**Triterpenes. LXXX. Further transformation of elemic acid.** L. Ruzicka, E. Rey, M. Spillmann, and H. Baumgartner (*Helv. Chim. Acta*, 1943, **26**, 1659—1671).—Various formulæ are tentatively advanced to explain the relationships of the elemic acids which cannot be brought into line with the proposals of Bilham *et al.* (A., 1942, II, 418). Elemenic acid is converted by  $\text{SOCl}_2$  in boiling abs. hexane into the corresponding *chloride*, m.p. 115—116°, reduced ( $\text{H}_2$ -Pd-BaSO<sub>4</sub> in PhMe at 90—100°) to *elemenal* (I), m.p. 139—139.5°,  $[\alpha]_D + 3.6$ . This is converted (Na in  $\text{C}_5\text{H}_{11}\text{OH}$  and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  at 180°) into non-cryst. *elemene*,  $[\alpha]_D - 9.83$ , which gives a yellow colour with  $\text{C}(\text{NO}_2)_4$ ; the *azine*, m.p. 214—214.5°, of (I) is occasionally obtained. *iso*Elemenic acid is similarly converted through its *chloride*, m.p. 126—127°,  $[\alpha]_D - 45.2$ , into *isoelemenal*, m.p. 181.5—182°,  $[\alpha]_D - 55.8$  (oxime, m.p. 110—111°; *azine*, m.p. 205—206°), and thence into *isoelemene*, m.p. 92—93°,  $[\alpha]_D - 77.8$ . Ozonisation of *Me* acetyl $\alpha$ -elemenolate in AcOH and decomp. of the ozonide with hot  $\text{H}_2\text{O}$  yields 95% of neutral, difficultly volatile material separated chromatographically into an  $\alpha\beta$ -unsaturated *ketone* (II),  $\text{C}_{33}\text{H}_{52}\text{O}_5$ , m.p. 177—178°,  $[\alpha]_D - 36.3$ , *Me* acetyl $\alpha$ -elemendionolate (III), m.p. 146—147°,  $[\alpha]_D - 26.3$ , and a compound (IV),  $\text{C}_{33}\text{H}_{54}\text{O}_6$ , m.p. 211—213°, probably a mol. oxide or a diketone. (II) and (III) but not apparently (IV) are obtained after ozonisation in  $\text{CHCl}_3$ . Oxidation of acetyl $\alpha$ -elemenic acid by  $\text{CrO}_3$  in AcOH at 70° leads to *iso*acetyl $\alpha$ -elemenic acid, m.p. 261.5—262°,  $[\alpha]_D - 28.3$ ; the *Me* ester, m.p. 146—147°,  $[\alpha]_D - 25.8$ , is hydrogenated ( $\text{PtO}_2$  in AcOH at room temp.) to the  $\alpha\beta$ -unsaturated *ketodihydroxy-ester*,  $\text{C}_{33}\text{H}_{52}\text{O}_6$ , m.p. 266—266.5°,  $[\alpha]_D - 56.4$ , and a *substance*, m.p. 122—124°, both compounds give an intense yellow colour with  $\text{C}(\text{NO}_2)_4$ . Acetyl $\alpha$ -elemadienolic acid is converted by  $\text{SOCl}_2$  in boiling hexane into the *chloride*, m.p. 209—210°,  $[\alpha]_D - 120.6$ . A  $\text{OH}\cdot\text{CH}$  compound from *Me* *iso*-elemenolate could not be obtained by the action of  $\text{NaOEt}$  and  $\text{HCO}_2\text{C}_5\text{H}_{11}$ -*iso* at 20° or 0° or by addition of finely-divided Na in  $\text{Et}_2\text{O}$  to the reactants in abs. EtOH. M.p. are corr. (vac.).  $[\alpha]_D$  are in  $\text{CHCl}_3$ . H. W.

**Sapogenins.**—See B., 1943, III, 280.

## VI.—HETEROCYCLIC.

**Preparation of 3-alkylchromones. Effect of substitution on the reactivity of the 2-methyl group in chromones.** A. Zaki and R. C. Azzam (*J.C.S.*, 1943, 434—435).—2-Methoxy-4-methylbenzoylacetone (I), m.p. 52°, prepared from the corresponding acetophenone and Na-EtOAc, with boiling HI gives 2 : 7-dimethylchromone, which with anisaldehyde in EtOH-NaOEt gives 4'-methoxy-2-styryl-7-methylchromone, m.p. 150°. The following are similarly obtained from the appropriate reagents:  $\alpha$ -2-methoxy-4-methylbenzoyl- $\alpha$ -methylacetone, b.p. 190—192°/20 mm. ( $\alpha$ -ethylacetone, b.p. 197—200°/20 mm.,  $\alpha$ -n-propylacetone, b.p. 206—210°/20 mm.,  $\alpha$ -n-butylacetone, b.p. 207—210°/10 mm., and  $\alpha$ -n-amylacetone, b.p. 215—220°/10 mm.); 2 : 3 : 7-trimethylchromone, 2 : 7-dimethyl-3-ethyl-, m.p. 51° (lit., liquid), -3-n-propyl-, m.p. 56—57°, -3-n-butyl-, and -3-n-amyl-chromone; 4'-methoxy-2-styryl-3 : 7-dimethyl-, m.p. 123°, and -7-methyl-3-ethyl-chromone, m.p. 114°; 4'-nitro-2-styryl-7-methyl-3-n-propyl-, m.p. 176—177°, -3-n-butyl-, m.p. 168—170°, and -3-n-amyl-chromone, m.p. 173—174°;  $\alpha$ -2-methoxy-4-methylbenzoyl- $\alpha$ -benzylacetone, m.p. 67—68°; 3-benzyl-2 : 7-dimethyl-, m.p. 95°, and 4'-methoxy-2-styryl-3-benzyl-7-methyl-chromone, m.p. 176°. NaOEt and (I) in EtOH give a mixture of forms of  $\alpha$ -benzoyl- $\alpha$ -2-methoxy-4-methylbenzoylacetone, m.p. 134—151°. F. R. S.

**Improved syntheses of 7-hydroxy- and 5 : 7-dihydroxy-flavanone.** S. Fujise and H. Tatsuta (*Ber.*, 1941, **74**, [B], 275—278; cf. A., 1934, 416).—5 : 7-Dihydroxyflavanone (I), m.p. 170—175°, is obtained from phloroglucinol,  $\text{CHPh}\cdot\text{CH}\cdot\text{COCl}$ , and  $\text{AlCl}_3$  in  $\text{PhNO}_2$ ; resorcinol, similarly treated, affords 7-hydroxyflavanone (II), m.p. 182.5—184.5° (pure 186—188°), and 2' : 4'-dihydroxychalkone, m.p. 146°. (I), but not (II), may be purified by vac. sublimation (at 0.007 mm.), giving (I), m.p. 199—200°. Chromatographic methods of purification have also given useful results. J. W.A.

**Constituents of *Ampelopsis meliaefolia*, Kudo (Haku-Tya).** M. Kotake and T. Kubota (*Annalen*, 1940, **544**, 253—271).—The leaves of this plant yield to hot  $\text{H}_2\text{O}$  a mixture, whence basic Pb acetate removes myricetin and *ampelopsin* (I) (7.4%), +2.5 $\text{H}_2\text{O}$ , m.p. 245—246° (*hexa*-acetate, m.p. 174—175°, and -benzoate, m.p. 174°). (I) is shown, as follows, to be 3 : 5 : 7 : 3' : 4' : 5'-hexahydroxyflavanone. With  $\text{CH}_2\text{N}_2-\text{Et}_2\text{O}$  it gives a *Me*<sub>4</sub> (II), m.p. 168°, and 5 : 7 : 3' : 4' : 5'-*Me*<sub>5</sub> ether (III), m.p. 194—195° [acetate, m.p. 156°; also obtained from (II) by  $\text{CH}_2\text{N}_2$ ].  $\text{MeI}-\text{K}_2\text{CO}_3-\text{COMe}_2$  also gives (III), but  $\text{Me}_2\text{SO}_4-\text{KOH}-\text{MeOH}$  gives the *Me*<sub>6</sub> ether (IV), m.p. 190—191°.  $\text{KOH}$  at 140—210° converts (I) into  $\alpha$ - $\text{C}_6\text{H}_3(\text{OH})_3$  and gallic acid (V). With  $\text{KMnO}_4-\text{H}_2\text{O}-\text{C}_6\text{H}_6$ , (III) gives the *Me*<sub>3</sub> ether of (V). In hot  $\text{KOH}-\text{MeOH}-\text{H}_2\text{O}$ , (IV) gives 2'-hydroxy- $\alpha$  : 3 : 4 : 5 : 4' : 6'-hexamethoxychalkone (VI), m.p. 147° (orange-yellow  $\text{FeCl}_3$  colour; adds Br), converted by  $\text{Me}_2\text{SO}_4-25\%$   $\text{KOH}-\text{MeOH}$  into the *Me*<sub>7</sub>

**derivative**, m.p. 129—130°, and synthesised from 2:4:6:1-OH-C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>·CO·CH<sub>2</sub>·OMe and 3:4:5:1-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>·CHO in KOH-aq. EtOH at room temp. (later 30—40° and then 50—60°). Heating (III) in 10% KOH-EtOH-H<sub>2</sub> for 1 hr. gives a substance, m.p. 129—130°, pentamethylmyricetin, and 3:5-dimethoxy-2:3':4':5'-trimethoxybenzylidene-1:2-dihydrobenzofuran, m.p. 162—163°. Heating (III) in 10% KOH-MeOH for 3 min. gives *epi-ampelopsin* Me<sub>3</sub> (VII), m.p. 170—171°, and thence (Me<sub>2</sub>SO<sub>4</sub>) the Me<sub>3</sub> ether, m.p. 120°, both obtained also from (VI) by HCl-EtOH-H<sub>2</sub>O under appropriate conditions. 10% KOH at 100° (1 hr.) converts (VII) into pentamethylampelopsic acid, 2:4:6:1-OH-C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>·C(OH)(CO<sub>2</sub>H)·CH<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-1:3:4:5, very readily converted into the lactone, m.p. 158—159°, and with CH<sub>2</sub>N<sub>2</sub>-Et<sub>2</sub>O giving *Me hexamethylampelopsate*, m.p. 150—151° (derived acid, m.p. 140°). Alcoholic acid or alkali dehydrates these products to *pentamethylanhidroampelopsolactone* (VIII), m.p. 159—160°, and *Me hexamethylanhidroampelopsate*, 2:4:6:1-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>·C(CO<sub>2</sub>Me):CH·C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-1:3:4:5, m.p. 112—113°, hydrolysed to the acid (IX), m.p. 159—160° (Et ester, m.p. 150—151°), and thence by decarboxylation 2:4:6:3':4':5'-hexamethylchalcone, m.p. 143—144°. O<sub>3</sub> converts (VIII) or (IX) into 3:4:5:1-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>·CHO. (III) is dehydrogenated by Pd-CHPh·CH·CO<sub>2</sub>H at 170—175° or H<sub>2</sub>O<sub>2</sub>-NaOH-MeOH-H<sub>2</sub>O to 3-hydroxymyricetin 5:7:3':4':5'-Me<sub>3</sub> ether; by the former method (IV) gives a compound, C<sub>21</sub>H<sub>22</sub>O<sub>8</sub>, m.p. 145—146°. (I) has α = 0; it and the *epi*-derivatives are *dl*-forms of C<sub>2-3</sub> stereoisomerides.

R. S. C.

**Constitution of calycopterin, yellow colouring matter of the leaves of *Calycopteris floribunda*.** R. C. Shah, V. V. Virkar, and K. Venkataraman (*J. Indian Chem. Soc.*, 1942, 19, 135—138).—Calycopterin (*dibenzyl ether*, m.p. 185°) with Me<sub>2</sub>SO<sub>4</sub> yields 3:5:6:7:8:4'-hexamethoxyflavone (I), but with CH<sub>2</sub>N<sub>2</sub> in Et<sub>2</sub>O gives 5-hydroxy-3:6:7:8:4'-pentamethoxyflavone, m.p. 124° (acetate, m.p. 107°; sparingly sol. K and Na salts; green colour with FeCl<sub>3</sub>) [also obtained by partial demethylation (50% HBr-AcOH at room temp.) of (I)], and is therefore 5:4'-dihydroxy-3:6:7:8-tetramethoxyflavone. 3-Methoxyflavone is demethylated by anhyd. AlCl<sub>3</sub> at 100°, or by HBr-AcOH at 100°, but not at room temp.

A. Li.

**Kostanecki-Robinson reaction. V. Benzoylation of some *o*-hydroxy-ketones.** P. L. Trivedi, S. M. Sethna, and R. C. Shah (*J. Indian Chem. Soc.*, 1943, 20, 171—172; cf. A., 1942, II, 60).—Resacetophenone, 2-acetylresorcinol, and phloracetophenone are benzoylated to 7- (cf. lit.), 5-, m.p. 234—235°, and 5:7-di-benzoyloxy-3-benzoylflavone, m.p. 167—168°, respectively. The OBz groups are then removed smoothly by conc. H<sub>2</sub>SO<sub>4</sub> (5:7-dihydroxy-3-benzoylflavone has m.p. 145—146°) leaving the C-Bz groups intact. Subsequent heating with KOH-EtOH gives 7-, 5-, and 5:7-di-hydroxyflavone, respectively.

S. A. M.

**Parachors and constitution of pyrones.**—See A., 1943, I, 299.

**Tetrahydrodibenzopyrans.**—See B., 1943, II, 342.

**Natural coumarins. LVI. Constitution of sphondin.** E. Späth and H. Schmid (*Ber.*, 1941, 74, [B], 595—598).—Sphondin (I) (A., 1936, 860) is not identical (mixed m.p.) with bergapten or *allobergapten*. With O<sub>3</sub> in CHCl<sub>3</sub> at 0° (I) gives 7-hydroxy-6-methoxycoumarin-8-aldehyde (II), m.p. 191.5—192.5°, also prepared from scopoletin and (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> in AcOH. Crude (II) [from (I)] and 1% H<sub>2</sub>O<sub>2</sub> in 0.05N-NaOH at 18° give fraxetin [7:8-dihydroxy-6-methoxycoumarin]. (I) is, therefore, 6-methoxy-7:8-2':3'-furano-coumarin.

H. B.

**Formation of 2:4-dimethyl-1:3-benzdioxins and their fission to *o*-vinylphenols.** E. Adler, H. von Euler, and G. Gie (*Arkiv Kemi, Min., Geol.*, 1943, 16, A, No. 12, 20 pp.).—*aa*-Di-6-hydroxy-*m*-tolyl-ethane, m.p. 141° (diacetate, m.p. 136—137°), obtained by the action of conc. HCl on a cold solution of *p*-cresol (4 mols.) and MeCHO (1 mol.) in EtOH, CHMe(C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>·OH-3:5:6)<sub>2</sub>, CHMe(C<sub>6</sub>H<sub>4</sub>·OH-*p*)<sub>2</sub>, and CHMe(C<sub>6</sub>H<sub>3</sub>Me·OH-3:4)<sub>2</sub> are converted by dry distillation under diminished pressure over frankonite into the corresponding vinylphenol, which invariably undergoes disproportionation when its separation from the large proportion of phenols produced simultaneously is attempted by distillation under atm. pressure; the final products are resins and the corresponding ethylphenol. 2:4:6:8-Tetramethyl-1:3-benzdioxin (I), m.p. 43.5°, is obtained in 30% yield when a solution of *m*-4-xylene (0.5 mol.) and MeCHO (or paracetaldehyde) (1 mol.) in C<sub>6</sub>H<sub>6</sub> is kept over 8N-HCl for 3 days at room temp. Under similar conditions *p*-cresol affords 2:4:6-trimethyl-1:3-benzdioxin (II), b.p. 115—120°/15 mm., m.p. 37°, in 40% yield and PhOH in Et<sub>2</sub>O gives 2:4-dimethyl-1:3-benzdioxin (III), b.p. 90—95°/15 mm. (I) is converted by HCl in boiling EtOH, or by heating at 220—230° or at 120—150° in presence of frankonite, into 2-2'-hydroxy-3':5'-dimethylphenyl-4:6:8-trimethylchroman (IV), m.p. 131.5°, converted by Me<sub>2</sub>SO<sub>4</sub>-NaOH in aq. MeOH into the Me ether, m.p. 147°, and by Ac<sub>2</sub>O containing a little conc. H<sub>2</sub>SO<sub>4</sub> at room temp. into *α*-di-(2-acetoxy-3:5-dimethylphenyl)-*n*-butyl acetate, m.p. 112°. Passage of (I), (II), or (III) in N<sub>2</sub> or steam through a glass, porcelain, or metal tube at (best) 550°, 600—650°, or 400—

450° respectively gives 2:4-dimethyl-6- (V), b.p. 108°/12 mm., m.p. 43°, and 4-methyl-2-vinylphenol (VI), b.p. 116—117°/15 mm., 74°/1 mm., and *o*-vinylphenol. (V) sublimes readily at room temp. (V) is transformed by CH<sub>2</sub>Cl·CO<sub>2</sub>H and 27% NaOH into 3:5:7-trimethylcoumaran-2-carboxylic acid (or 6:8-dimethylchroman-2-carboxylic acid), m.p. 99°. (V) is converted by Br in Et<sub>2</sub>O followed by aq. NaHCO<sub>3</sub> into the (?) trimeric quinonemethide, (C<sub>9</sub>H<sub>9</sub>OBr)<sub>3</sub>, m.p. 133°. (V) passes into (IV) when heated at 100° for 10 hr. (VI) is partly transformed by distillation under 1 mm. pressure into a viscous dimeride which passes into an alkali-insol. resin when distilled. With CH<sub>2</sub>Cl·CO<sub>2</sub>H and NaOH (VI) affords 4-methyl-2-vinylphenoxyacetic acid, m.p. 135°.

H. W.

**Natural coumarins. LV. Synthesis of luvangetin.** E. Späth and H. Schmid (*Ber.*, 1941, 74, [B], 193—196; cf. *ibid.*, 1940, 73, 1361).—1:3:2-C<sub>6</sub>H<sub>3</sub>(OH)<sub>2</sub>·OMe, Zn(CN)<sub>2</sub>, and dry HCl in abs. Et<sub>2</sub>O afford 2:4-dihydroxy-3-methoxybenzaldehyde, m.p. 85.5—86.5°, which gives daphnetin (I), m.p. 161°, by a Perkin reaction. (I) and CH<sub>2</sub>C·CMe<sub>2</sub>·OH at 200° (sealed tube) give a small yield of luvangetin (II), m.p. 106—107°, after

J. Wa.

removal of unchanged (I).

**Vat dyes (thianthrens, phenoxthionins, etc.).**—See B., 1943, II, 344.

**Substituted 4-aminopiperidines. III. V. Hahn, E. Cerkovnikov, and V. Prelog (*Helv. Chim. Acta*, 1943, 26, 1132—1142).**—Tetrahydropyran-4-carboxylamide is converted by Br-NaOH into 4-aminotetrahydropyran (hydrochloride, m.p. 218—219°; *picrate*, m.p. 175—175.5°; *Ac* derivative, m.p. 149—150°), from which *α*-*di*-chloro-*γ*-aminopentane hydrochloride is obtained by the action of conc. HCl at 120—130°. It is converted by NH<sub>2</sub>Ph-EtOH at 150—160° into 4-amino-1-phenylpiperidine, b.p. 125—126°/0.7 mm. (*dipicrate*, m.p. 201—202°; dihydrochloride, m.p. 264—265°), in 67% yield. 4-Dimethyltetrahydropyran hydrochloride (corresponding *picrate*, m.p. 174.5—175.5°) is similarly transformed into *α*-*di*-chloro-*γ*-dimethylaminopentane hydrochloride, m.p. 127—128° (corresponding *picrate*, m.p. 124—125°), which yields 4-dimethylamino-1-phenylpiperidine (I), b.p. 128—132°/1 mm., m.p. 47.5—48.5° (dihydrochloride, m.p. 252—253°; *dipicrate*, m.p. 203—204°). 4-Hydroxy-1-phenylpiperidine hydrochloride, m.p. 193.5—194.5° (corresponding *hydriodide*, m.p. 73—74°), is transformed by SOCl<sub>2</sub> in CHCl<sub>3</sub> into the glassy 4-chloro-1-phenylpiperidine hydrochloride (corresponding *picrate*, m.p. 163.5—164.5°), which is converted by anhyd. NHMe<sub>2</sub> in abs. EtOH at 150° into (I) in 20% yield. 4-Iodo-1-phenylpiperidine *hydriodide*, m.p. 189—190°, and piperidine in boiling abs. EtOH give 4-piperidino-1-phenylpiperidine, b.p. 165—168°/1 mm., and 1-phenyl-1:2:3:4-tetrahydropyridine, b.p. 125—130°/1 mm., in 27% and 47% yield respectively. 1-*p*-Tolyl-4-pyridone is reduced by Na and EtOH to 4-hydroxy-1-*p*-tolylpiperidine, b.p. 160—162°/0.25 mm., m.p. 88.5—89° (*hydrobromide*, m.p. 172—173°), transformed by 68% HBr at 175—185° into 4-bromo-1-*p*-tolylpiperidine, m.p. 78—79° [*hydrobromide* (II), m.p. 206.5—207°; *picrate*, m.p. 158°]. 4-Iodo-1-*p*-tolylpiperidine, m.p. 92—93° (*hydriodide*, m.p. 92—93°), is described. Both compounds are converted by NHMe<sub>2</sub> in abs. EtOH at 140—150° into 4-dimethylamino-1-*p*-tolylpiperidine in 36% yield. (II) and piperidine in abs. EtOH at 140—150° give 1-*p*-tolyl-1:2:5:6-tetrahydropyridine, b.p. 116—117°/0.1 mm. (*picrate*, m.p. 130—131°), in 56% yield and 4-piperidino-1-*p*-tolylpiperidine, b.p. 170—175°/0.1 mm., m.p. 83.5—84.5° (dihydrochloride, m.p. 264—266°; *dipicrate*, m.p. 205—206°), in 24% yield. (II) and NH<sub>2</sub>Ph in abs. EtOH at 140—145° afford 4-anilino-1-*p*-tolylpiperidine (amorphous *dihydrochloride*; *dipicrate*, decomp. 205—210°; *direineckate*, decomp. 200—205°). 4-Hydroxy-1-2':4'-dimethylphenylpiperidine, b.p. 160—161°/0.3 mm. (*hydrobromide*, m.p. 189°; *phenylurethane*, m.p. 128°), is obtained by reduction (Na-EtOH) of 1-2':4'-dimethylphenyl-4-pyridone and is converted into 4-bromo-1-2':4'-dimethylphenylpiperidine which does not crystallise or give cryst. salts; its *hydrobromide* affords 4-piperidino-1-2':4'-dimethylphenylpiperidine, a viscous liquid, b.p. 220—222°/1 mm. (*dipicrate*, m.p. 186.5—188°; *dipicrolonate*, m.p. 178—179°). Chelidonic acid and *p*-OMe-C<sub>6</sub>H<sub>4</sub>-NH<sub>2</sub> at 180° afford 1-*p*-anisyl-4-pyridone, m.p. 185—186° (*picrate*, m.p. 188—189°); the *hydrochloride*, m.p. 159—161°, is reduced to 4-hydroxy-1-*p*-anisylpiperidine, b.p. 180—182°/0.2 mm., m.p. 76.5—77°, the *hydrobromide*, m.p. 225—226°, of which is transformed by 68% HBr at 175—185° into 4-bromo-1-*p*-hydroxyphenylpiperidine, m.p. 129—130° (*hydrobromide*, m.p. 222.5—223.5°), converted by piperidine in EtOH at 140—145° into the non-cryst. 4-piperidino-1-*p*-hydroxyphenylpiperidine [*dipicrate*, m.p. 189—191° (decomp.)]; *direineckate*, m.p. 191—193° (decomp.) and by NH<sub>2</sub>Ph in EtOH at 140—145° into 4-anilino-1-*p*-hydroxyphenylpiperidine (*dipicrate*, decomp. 205—210°; *direineckate*, decomp. 205—210°). H. W.

**Novel preparation of *α*-hydroxypyrroles; example of an intramolecular correlated reaction.** W. Siedel [with, in part, K. Theis] (*Annalen*, 1943, 554, 144—161).—A general method of preparing *α*-OH-pyrroles depends on simultaneous exchange of Br for OH and decarboxylation; if the latter is prevented, *e.g.*, by esterification,

replacement of Br does not occur. 3-Methyl-4-ethylpyrrole-2-carboxylic acid is converted by Br in cold AcOH into the 5-Br-derivative (I), which is converted by MeOH—conc. HCl into 5-methoxy-3-methyl-4-ethylpyrrole (II), b.p. 79—80°/10 mm., 85°/13 mm. [picrate, m.p. 152° (corr.); 5-methoxy-3-methyl-4-ethylpyrroleazobenzenesulphonic acid hydrochloride, m.p. 180—182°], and a non-cryst. compound, b.p. 127°/2.5 mm. Under similar conditions 5-ethoxy-, b.p. 95°/11 mm., 5-propoxy-, b.p. 104—105°/11 mm. (these do not give picrates or azo-dyes), and 5-benzyloxy-, m.p. 136°, -3-methyl-4-ethylpyrrole are obtained. 5-Hydroxy-3-methyl-4-ethylpyrrole (isohydroxyopsopyrrole) (III), b.p. 156°/11 mm., 130—133°/3 mm., forms very volatile and hygroscopic crystals, m.p. 58—60°; it is obtained from (II) and saturated HCl—MeOH at 100° or from (I) and conc. aq. HCl. It does not give a picrate or azo-dye but affords a very hygroscopic hydrochloride, m.p. 78°, softens at 60°. Attempts to introduce the CHO into (III) by successive treatments with MgEtBr and HCO<sub>2</sub>Et give isopsopyrryl formate (IV), b.p. 116—117°/3 mm., which does not give a picrate or an azo-dye and is hydrolysed by alkali to (III); isopsopyrryl acetate has b.p. 118°/2 mm., 121—122°/3 mm. With HCN—HCl in Et<sub>2</sub>O (III) gives an unidentified compound, b.p. 126—127°/3 mm. The proof that OH in (III) has replaced Br and not CO<sub>2</sub>H of (I) is afforded by the prep. of Me isoxanthobilirubate, m.p. 205°, from (IV) and β-5-aldehydo-2:4-dimethylpyrrole-3-propionic acid in boiling Ac<sub>2</sub>O followed by hydrolysis and esterification (CH<sub>2</sub>N<sub>2</sub>) and of Me isoneoxanthobilirubate, m.p. 206°, from (III) and aldehydo-opsopyrrolecarboxylic acid (V) followed by HCl—MeOH. Et 2:3:4-trimethylpyrrole-5-carboxylate in abs. Et<sub>2</sub>O is transformed by SO<sub>2</sub>Cl<sub>2</sub> at room temp. into Et 2-carboxy-3:4-dimethylpyrrole-5-carboxylate, which passes at 220° followed by distillation at 340°/10 mm. into Et 3:4-dimethylpyrrole-5-carboxylate, m.p. 95—96°; the corresponding acid, sublimes without melting at 180°, is converted by Br in AcOH at 0° into 2-bromo-3:4-dimethylpyrrole-5-carboxylic acid, no m.p., transformed by conc. HCl into 2-hydroxy-3:4-dimethylpyrrole, m.p. 135° (decomp.). This with (V) and NaOH in aq. MeOH at 100° affords 5-hydroxy-3:3':4-trimethylpyrromethene-4'-propionic acid, m.p. 289° (corr.) [Me ester, m.p. 223° (corr.), 234° (microscope)]. (I) and (V) in MeOH and 48% HBr yield Me 5-carbomethoxy-4:3'-dimethyl-3-ethylpyrromethene-4'-propionate hydrobromide, m.p. 173° (microscope), softens at 168°; the free base affords a picrate, m.p. 138°, and salts, C<sub>38</sub>H<sub>46</sub>O<sub>8</sub>N<sub>4</sub>Cu, m.p. 138°; and C<sub>38</sub>H<sub>46</sub>O<sub>8</sub>N<sub>4</sub>Zn, m.p. 151°.

**Adermine.**—See B., 1943, III, 256.

**Preparation of alkoxy-o-aminophenylacetic acids, alkoxy-oxindoles and -isatins.** G. Hahn and M. R. Tulus (Ber., 1941, 74, [B], 500—519; cf. A., 1939, II, 387).—isoVanillin cyanohydrin and boiling Ac<sub>2</sub>O—NaOAc give the diacetate, m.p. 84°, converted by the prolonged action of HCl in C<sub>6</sub>H<sub>6</sub> into α-chloro-α-3-acetoxy-4-methoxyphenylacetamide, m.p. 135—136°; the -α-3:4-dimethoxy-, m.p. 145°, and -methylenedioxy-phenyl, m.p. 107°, analogues are similarly obtained. These amides with HNO<sub>3</sub> (d 1.4) at <0° give α-chloro-α-6-nitro-3-acetoxy-4-methoxy- (I), m.p. 137°, -α-6-nitro-3:4-dimethoxy- (II), m.p. 186° (decomp.), and -α-6-nitro-3:4-methylenedioxy-phenylacetamide (III), m.p. 168°, respectively. Reduction of (II) with H<sub>2</sub>—Pd—AcOH affords 5:6-dimethoxyoxindole (IV) (98%), m.p. 204—205°, with H<sub>2</sub>—Pd—AcOH—HCl (2 mols.) gives (IV) (25%) and 6-amino-3:4-dimethoxyphenylacetamide, m.p. 147° [as hydrochloride (V) (72%), m.p. 214°, converted by short treatment with warm AcOH into (IV)]; the amide is hydrolysed by 2N-Na<sub>2</sub>CO<sub>3</sub> at 70° to (IV)], with H<sub>2</sub>—PtO<sub>2</sub>—AcOH affords (IV) (22%) and (V) (76%), with H<sub>2</sub>—PtO<sub>2</sub>—AcOH—HCl (2 mols.) gives (IV) (15%) and (V) (80%), and with H<sub>2</sub>—Pd—MeOH affords (IV) (11%) and (V) (77%). Under the same reduction conditions (III) gives 94 and 0, 78 and 15, 88 and 7, 73 and 22, and 30 and 51%, respectively, of 5:6-methylenedioxyoxindole, m.p. 218° (decomp.), and 6-amino-3:4-methylenedioxyphenylacetamide hydrochloride, decomp. 190° (free base, m.p. 146—147°). Oxindole formation does not occur on reduction of (I) but the intermediate NH<sub>2</sub>-amide undergoes hydrolysis; H<sub>2</sub>—Pd—AcOH gives 6-hydroxy-3-acetoxy-4-methoxy-, m.p. 143°, and H<sub>2</sub>—PtO<sub>2</sub>—AcOH affords 3:6-dihydroxy-4-methoxy-phenylacetamide, m.p. 152—153°. Reduction of o-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CO<sub>2</sub>H, 3:4:6:1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)·CH<sub>2</sub>·CO<sub>2</sub>H, and 3:4:6:1-CH<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)·CH<sub>2</sub>·CO<sub>2</sub>H (VI) with H<sub>2</sub>—Pd—AcOH—HCl gives, as expected, mainly the NH<sub>2</sub>-acid hydrochlorides, which are thermolabile. The free NH<sub>2</sub>-acids are best obtained by reduction with H<sub>2</sub>—Pd—MeOH and adding C<sub>6</sub>H<sub>6</sub> to the resulting solution; they can be diazotised and coupled with β-C<sub>10</sub>H<sub>7</sub>·OH. 6-2'-Hydroxy-1'-naphthaleneazo-3:4-dimethoxy-, m.p. 214—215°, and -3:4-methylenedioxy-phenylacetic acid, decomp. 228—229°, are described. 3:4:1-CH<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·CH<sub>2</sub>·CO·NH<sub>2</sub> and HNO<sub>3</sub> at 0° give 6-nitro-3:4-methylenedioxyphenylacetamide, m.p. 218—219°, hydrolysed (6N-HCl) to (VI), new m.p. 184—185°, also obtained by nitration of homopiperonylic acid. Isatin (1 mol.) and (IV) (1 mol.) in AcOH—12N-HCl give 5:6-dimethoxyindigotin, decomp. 334°. Excess of Br and (IV) in boiling CHCl<sub>3</sub> afford a tribromo-oxindole, m.p. 187°, converted by boiling 2N-NaOH into 7-bromo-6-hydroxy-5-methoxyisatin, decomp. 280° (darkens 250°). NaNO<sub>2</sub> and (IV) in AcOH give 5:6-dimethoxyisatin-3-oxime, m.p. 213—214° (unaffected by dil. acid, alkali, AcOH—

H<sub>2</sub>O<sub>2</sub>, or short treatment with AcOH—H<sub>2</sub>SO<sub>4</sub>; boiling acid ultimately causes demethylation), reduced (H<sub>2</sub>, Pd, 80% HCO<sub>2</sub>H, H<sub>2</sub>SO<sub>4</sub>) to 3-amino-5:6-dimethoxyoxindole; the hydrochloride of this with hot 2N-NaOH in air affords 5:6-dimethoxyisatin, decomp. 250—252° (darkens 220°). 5:6-Methylenedioxyisatin-3-oxime, m.p. 242°, similarly gives 3-amino-5:6-methylenedioxyoxindole hydrochloride, decomp. 200°, and thence 5:6-methylenedioxyisatin, decomp. 284°.

**Synthesis of 2-pyridyl- and 2-quinolyl-dialkylcarbinols.** B. Emmer and E. Pirot (Ber., 1941, 74, [B], 714—719; cf. A., 1939, II, 387).—Addition of HgCl<sub>2</sub> in cyclopentanone to Mg in anhyd. C<sub>5</sub>H<sub>5</sub>N gives (cf. loc. cit.) 1-2'-pyridylcyclopentanol, b.p. 137—138°/13 mm., m.p. 84°, and 1:1'-dihydroxy-1:1'-dicyclopentyl. Similarly, cyclohexanone gives 1-2'-pyridylcyclohexanol (I), b.p. 143—144°/13 mm., m.p. 43°, and 1:1'-dihydroxy-1:1'-dicyclohexyl. With camphor (synthetic) Al must be used for Mg; 5% of 2'-pyridylborneol, b.p. 155—157°/12 mm., is thus obtained. Dehydration (KHSO<sub>4</sub> at 150° conc. H<sub>2</sub>SO<sub>4</sub> at 100°) of (I) gives (?) 1-2'-pyridyl-Δ<sup>1</sup>-cyclohexene, b.p. 259°. With quinoline, use of much Al and HgCl<sub>2</sub> is necessary: COMe<sub>2</sub> thus affords 2-quinolyl dimethylcarbinol, m.p. 67° (picrate, m.p. 110°), also obtained from Me quinoline-2-carboxylate and MgMeI; COMeEt gives 2-quinolyl methyl ethylcarbinol, b.p. 126—128°/0.1 mm. (picrate, m.p. 92—93°); cyclohexanone gives 1-2'-quinolylcyclohexanol, m.p. 66° (picrate, m.p. 145°). The Mg or Al is activated with I. No reaction occurs with 2:6-dimethylpyridine, COMe<sub>2</sub>, Al, and HgCl<sub>2</sub>. The reaction cannot be applied to CO-esters, diketones, and RCHO; unsaturated ketones and CHPh:NPh (for C<sub>5</sub>H<sub>5</sub>N) are resinified. C<sub>10</sub>H<sub>8</sub> (for C<sub>5</sub>H<sub>5</sub>N) does not react. It is unlikely that radicals play any part in the reaction; CRR'(MgCl)·OMgCl may be an intermediate.

H. B.

**Solution colours of phenol betaines of the quinoline series.** W. Schneider and A. Pothmann (Ber., 1941, 74, [B], 471—493).—7-Hydroxy-2-phenylquinoline-4-carboxylic acid is decarboxylated by distillation with Hg to 7-hydroxy-2-phenylquinoline (I), m.p. 229—230°, which with Me<sub>2</sub>SO<sub>4</sub> at 120—130° followed by aq. KI gives the methiodide (II), m.p. 223°. 7-Methoxy-2-phenylquinoline [from (I) and CH<sub>2</sub>N<sub>2</sub> or by decarboxylation of 7-methoxy-2-phenylquinoline-4-carboxylic acid, m.p. 238° (from PhCHO, AcCO<sub>2</sub>H, and m-anisidine in EtOH at 70—80°)] similarly gives a methiodide, m.p. 206°, converted by HBr (d 1.78) at 140° (sealed tube) followed by aq. KI into (II). A basic methiodide, (C<sub>16</sub>H<sub>13</sub>ON)<sub>2</sub>·HI, m.p. 216°, is obtained from (II) and Ag<sub>2</sub>O in cold H<sub>2</sub>O; in warm H<sub>2</sub>O, 7-hydroxy-2-phenylquinoline methyl betaine (+2H<sub>2</sub>O) (III), m.p. 85° (rapid), 253° (slow heating), results. 6-Methoxy-2-phenylquinoline-4-carboxylic acid, m.p. 237° (from PhCHO, AcCO<sub>2</sub>H, and p-anisidine), is demethylated (HBr) and then decarboxylated (Hg) to 6-hydroxy-2-phenylquinoline, m.p. 218°, the methiodide (+H<sub>2</sub>O), m.p. 110—111° (rapid), 188° (slow cautious heating), of which with Ag<sub>2</sub>O—H<sub>2</sub>O gives the impure betaine (+>1H<sub>2</sub>O), m.p. 165—166°. The colours of this and (III) in various solvents (detailed) are similar. It is immaterial for colour production whether quinonoid formation can occur or not. In accordance with this view the betaine (+4H<sub>2</sub>O), m.p. 85° (rapid), 217° (slow heating), from 2-p-hydroxyphenylquinoline methiodide (+H<sub>2</sub>O), m.p. 209—210°, and Ag<sub>2</sub>O—H<sub>2</sub>O shows the characteristic colour changes of phenol betaines. 2-p-Hydroxyphenylquinoline-4-carboxylic acid, m.p. 330°, is prepared from p-OH·C<sub>6</sub>H<sub>4</sub>·CHO, AcCO<sub>2</sub>H, and NH<sub>2</sub>Ph. Introduction of ·CH:CH· or ·CH:CH·CH:CH· between the quinoline and Ph rings causes a considerable deepening in colour. 2-p-Hydroxystyrylquinoline (IV) gives (cf. Vonderwahl, Diss., Genève, 1913) a methiodide (+H<sub>2</sub>O) (V), m.p. 256°, and an ethiodide (+EtOH) (VI), m.p. 231° [described by Vonderwahl as (V)] [readily obtained from 2-methylquinoline ethiodide (VII) and p-OH·C<sub>6</sub>H<sub>4</sub>·CHO in EtOH—piperidine]. With Ag<sub>2</sub>O or, better, short treatment with boiling aq. EtOH—NH<sub>3</sub>, (V) gives a basic methiodide, (C<sub>18</sub>H<sub>16</sub>ON)<sub>4</sub>·HI·6H<sub>2</sub>O, m.p. 149°, converted by aq. EtOH—NH<sub>3</sub> into the betaine (+3H<sub>2</sub>O; 0.5H<sub>2</sub>O lost rapidly in air; 1.5H<sub>2</sub>O lost in a desiccator), m.p. 212° (sinters 190°); (VI) (in AcOH) with excess of NaOH affords the ethyl betaine (+3H<sub>2</sub>O), m.p. 152°. The colours of both betaines are similar. The betaines (not isolated except in CHCl<sub>3</sub>) from 2-m-hydroxystyrylquinoline methiodide (+H<sub>2</sub>O), m.p. 244° (decomp.), and ethiodide (+H<sub>2</sub>O), m.p. 231°, show relatively lighter colorations (yellow changing to red; ? change of dissolved hydrate to anhydride) which are independent of temp., indicating the possibility of a quinonoid limiting state in hydroxyphenylquinoline derivatives. CH<sub>2</sub>PhCl and (IV) at 200—210° give the hydrochloride (+2H<sub>2</sub>O), m.p. 292° (lit. 264—266°), of (IV) and the impure benzylochloride. The latter with aq. NaOH in CHCl<sub>3</sub> affords the benzyl betaine (+H<sub>2</sub>O), m.p. 143—144° (softens from 130°), which shows a little deeper solution colours than the Me and Et analogues. 4-p-Hydroxystyrylquinoline methiodide (+1.5H<sub>2</sub>O), m.p. 131° or 260° (stable) (from the 4-Me derivative and p-OH·C<sub>6</sub>H<sub>4</sub>·CHO in EtOH—piperidine), gives (NaOH) the betaine (+3H<sub>2</sub>O), m.p. 234° (sinters from 207°), which are distinctly deeper in colour than the 2-derivatives. p-OMe·C<sub>6</sub>H<sub>4</sub>·CH:CH·CHO (VIII) could not be condensed with various quaternary iodides but with (VII) in EtOH—piperidine gives 2-δ-p-anisyl-Δ<sup>αγ</sup>-butadienylquinoline ethiodide, m.p. 259°, demethylated (aq. AcOH—HBr) to the

*p*-OH-ethiodide, m.p. 193—194°, which affords the impure betaine (+1.5H<sub>2</sub>O) (shows the expected deepening in colour). Attempted condensation of 4-methylquinoline ethiodide and (VIII) in HCO<sub>2</sub>H at 100° gave, unexpectedly, 4-methyl-1-ethylquinolinium tri-iodide, m.p. 91°. With some of the betaines studied, e.g., those from (V) and (VI), it is found that for solvents of decreasing solvating power there is an increasing depth in the colour; in PhMe, C<sub>6</sub>H<sub>5</sub>N, and dioxan the colours are displaced slightly towards the red and heating above room temp. produces no deepening. H. B.

**8-Hydroxyquinoline-5-sulphonamide.**—See B., 1943, III, 256.

**Syntheses and transformations of natural substances under conditions possible in the cell. VIII. Biogenesis of 1-benzyl-1:2:3:4-tetrahydroisoquinoline alkaloids.** Synthesis of 6:7-dihydroxy-1-3':4'-methylenedioxybenzyl-1:2:3:4-tetrahydroisoquinoline under conditions possible in the cell. C. Schöpf and W. Salzer (*Annalen*, 1940, 544, 1—30; cf. A., 1936, 1002; 1937, II, 526).—Contrary to Hahn *et al.* (A., 1937, II, 76), 1-benzyl-1:2:3:4-tetrahydroisoquinolines can be synthesised under "natural" conditions from Ar·[CH<sub>2</sub>]<sub>2</sub>·NH<sub>2</sub> and CH<sub>2</sub>Ar'·CHO provided that Ar has a group activating the *o*-position. Natural alkaloids containing Oalk in the Bz nucleus are formed by way of the OH-derivatives, which are alkylated after cyclisation. The condensation occurs at pH 3—7; at pH 7 it is extremely rapid (30% in 13 min.). Self-condensation of CH<sub>2</sub>Ar'·CHO occurs in acid solution, but at pH 7 is not rapid enough to interfere appreciably with the formation of the isoquinoline derivative. 3:4:1-CH<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·CH<sub>2</sub>·OH [prep. from piperonal by Al(OPr<sup>i</sup>)<sub>3</sub>·Pr<sup>i</sup>OH at 95°], m.p. 51°, b.p. 151°/13 mm., with SOCl<sub>2</sub>·CHCl<sub>3</sub>·C<sub>6</sub>H<sub>5</sub>N gives the chloride, b.p. 130°/13 mm., and thence (NaCN·EtOH·H<sub>2</sub>O) the nitrile, b.p. 164°/14 mm., and (alkali) homopiperonylic acid, m.p. 128°. This with 3:4:1-(CH<sub>2</sub>Ph·O)<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·[CH<sub>2</sub>]<sub>2</sub>·NCO (prep. *in situ* from the hydrazide by way of the azide) in boiling C<sub>6</sub>H<sub>6</sub> gives CO<sub>2</sub> and piperonyl-β-3':4'-dibenzylloxyphenylethylamide (74%), m.p. 119—121°, converted by PCl<sub>5</sub> in CHCl<sub>3</sub> at <0° and then room temp. into 6:7-dibenzylloxy-1-piperonyl-3:4-dihydroisoquinoline hydrochloride (70%), m.p. 205—207° [gives the methiodide (I), m.p. 204—205°, of the base], which with Zn dust in boiling 50% AcOH gives 6:7-dibenzylloxy-, sinters 105°, m.p. 108°, and with H<sub>2</sub>·PtO<sub>2</sub> and then Pd·BaSO<sub>4</sub> in MeOH gives 6:7-dihydroxy-1-piperonyl-1:2:3:4-tetrahydroisoquinoline (II), sinters 123°, m.p. 128° (decomp.) [hydrochloride (III), +2EtOH, m.p. 256° (decomp.); picrate, sinters 153°, m.p. 159° (decomp.)]. (III) is determined (95.5—99%) in presence of 3:4:1-(OH)<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·[CH<sub>2</sub>]<sub>2</sub>·NH<sub>2</sub>·HBr (IV) in much H<sub>2</sub>O by pptn. of the picrolonate, m.p. (anhyd.) 243° (decomp.) or (+xH<sub>2</sub>O) swells at 159°, m.p. 165—170° (turbid), decomp. 238—240°. With AgOAc and then Zn dust in aq. AcOH at the b.p. etc., (I) gives 6:7-dibenzylloxy-1-piperonyl-2-methyl-1:2:3:4-tetrahydroisoquinoline hydrochloride, +0.5H<sub>2</sub>O (retained at 60°/high vac.), m.p. 105—115°. Saffrole oxide (prep. by BzO<sub>2</sub>H in CHCl<sub>3</sub>; 50% yield), b.p. 149—150°/11 mm., in boiling 10% AcOH gives the glycol (90%), m.p. 82°, which with Pb(OAc)<sub>4</sub> gives homopiperonal (V). (V) is readily determined in H<sub>2</sub>O by pptn. of its semicarbazone, m.p. 180°. (V) is stable for 3 days at pH 3—5, but undergoes self-condensation in ~24 hr. at pH 7 or 1 hr. at pH 9. The rates of disappearance of (V) and formation of (II) from mixtures of (IV) (1 mol.) and (V) (1.1 mol.) in H<sub>2</sub>O (~0.01M.) are determined at pH 3—7 and 25°. (V) disappears faster than (II) is formed, particularly at pH 7; in such cases the semicarbazone is formed after heating but not in the cold; it is assumed that condensation gives initially and reversibly (OH)<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·[CH<sub>2</sub>]<sub>2</sub>·N·CH·CH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·CH<sub>2</sub>O<sub>2</sub> or irreversibly (II). 3:4:1-CH<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·CH<sub>2</sub>·CO·CO<sub>2</sub>H is determined in H<sub>2</sub>O as the *p*-nitrophenylhydrazone, m.p. 201°. The rate of its condensation with (IV) is faster at pH 7 than at pH 5, but in all cases much slower than that of (V). Thus, synthesis of isoquinoline alkaloids is by way of the aldehydes rather than of the pyruvic acids. R. S. C.

**Photographic sensitisers derived from quinaldine.** M. Q. Doja and D. Prasad (*J. Indian Chem. Soc.*, 1943, 20, 153—158; cf. A., 1943, II, 172).—*p*-NEt<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO and quinaldine methiodide, with piperidine in hot EtOH, give 2-*p*-diethylaminostyrylquinoline methiodide, m.p. 190°, yield 40%, range of photographic sensitisation 4200—6350 Å. and of uniformly intense sensitisation 4400—5250 Å. Corresponding figures for other alkiodides, obtained similarly, are: *B*, 230°, 76%, 4200—6400, 4350—5000 Å.; *Pr*<sup>a</sup>, 198°, 67%, 4250—6150, 4400—5000 Å.; *Bu*<sup>a</sup>, 111°, 31%, 4200—6350, 4350—5000 Å., respectively. Optical and dyeing properties are described. The syntheses have not been quite successful in producing a single sensitiser for panchromatic plates, owing to the failure to sensitise for a short region in the blue-green portion of the spectrum. Quinaldine *n*-propiodide, m.p. 145—146°, and *n*-butiodide, m.p. 193°, are new. S. A. M.

**Chemical constitution and antiplasmodic action. VI. Heterocyclic derivatives of 8-aminoquinoline and of 8-amino-6-methoxyquinoline.** E. Cerkovnikov, V. Prelog, and P. Stern (*Helv. Chim. Acta*, 1943, 26, 1180—1185).—8-Amino-6-methoxyquinoline, Br·[CH<sub>2</sub>]<sub>2</sub>·Br, and CaCO<sub>3</sub> in EtOH at 150° afford 8-piperidino-6-methoxyquinoline, b.p. 240°/0.8 mm., m.p. 57—58° (dihydrochloride, m.p. 141—142°); in absence of CaCO<sub>3</sub> hydrolysis of OMe occurs.

Under similar conditions Br·[CH<sub>2</sub>]<sub>2</sub>·Br yields 8-hexamethyleneimino-6-methoxyquinoline, b.p. 240—245°/0.7 mm. (dipicrate, m.p. 168—169°; dihydrochloride; dipicrolonate, m.p. 222—223°). Analogously O([CH<sub>2</sub>]<sub>2</sub>·Cl)<sub>2</sub> gives 8-morpholino-6-methoxyquinoline, b.p. 238°/0.5 mm. m.p. 122—123° (sulphosalicylate, m.p. 235—236°), and S([CH<sub>2</sub>]<sub>2</sub>·Cl)<sub>2</sub> yields 8-thiomorpholino-6-methoxyquinoline, b.p. 240—241°/0.3 mm. (picrate, m.p. 190—191°; hydrochloride, m.p. 218—219°). 8-4'-Aminopiperidino-6-methoxyquinoline, b.p. 205—209°/0.1 mm. [trihydrochloride (I), m.p. 219—220°; dipicrate, m.p. 209—210°], is derived from NH<sub>2</sub>·CH([CH<sub>2</sub>]<sub>2</sub>·Br)<sub>2</sub>·HBr. (I), KOH, and Cl·[CH<sub>2</sub>]<sub>2</sub>·NEt<sub>2</sub>·HCl in abs. EtOH at 140° yield 8-4'-γ-diethylamino-propylaminopiperidino-6-methoxyquinoline, b.p. 235°/0.2 mm. [tetrahydrochloride, m.p. 217—218° (decomp.)]. 8-4'-Dimethylaminopiperidino-6-methoxyquinoline, b.p. 225—230°/0.3 mm., gives a dipicrate, m.p. 208—209° (decomp.). Compounds which do not contain OH or OMe at C<sub>6</sub> are physiologically inactive. Of the remaining compounds only those are active which have at least one free H united to N; this is not necessarily united to the N atom directly attached to the quinoline nucleus. H. W.

**Synthesis of nitrogen-containing heterocyclic rings. XXI. Synthesis of dibenzquinolizine derivatives. IV. Synthesis of 2':3':2'':3''-tetramethoxy-1:2:6:9-tetrahydro-3:4:7:8-dibenzquinolizine.** S. Sugawara, K. Kodama, and H. Inagaki.

**XXII. Oxidation of β-phenylethylpyridinium salts. II.** S. Sugawara and H. Shigehara (*Ber.*, 1941, 74, [B], 455—459, 459—469).—XXI. Et β-keto-γ-3:4-dimethoxyphenylbutyrate [from 3:4:1-(OMe)<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·CH<sub>2</sub>·COCl and CHNaAc·CO<sub>2</sub>Et in Et<sub>2</sub>O followed by aq. NH<sub>3</sub>·NH<sub>4</sub>Cl] with 3:4:6:1-(OMe)<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>(NH<sub>2</sub>)·CHO in EtOH-piperidine at 29—30° gives Et 6:7-dimethoxy-2-3':4'-dimethoxybenzylquinoline-3-carboxylate, m.p. 140° (picrate, decomp. 179°; 1:2:3:4-H<sub>4</sub>-derivative, m.p. 94—95°, readily obtained by H<sub>2</sub>·PtO<sub>2</sub>-dil. HCl). The free acid, decomp. 230°, with Cu chromite in quinoline at 230—235° gives 6:7-dimethoxy-2-3':4'-dimethoxybenzylquinoline (I), m.p. 205° (decomp.) (sinters ~100°) (hydrochloride, decomp. 234°; picrate, decomp. 199—200°), which is only slowly reduced to the 1:2:3:4-H<sub>4</sub>-derivative, m.p. 99—100° [hydrochloride (II), decomp. 212—213°; 1-Bz derivative, m.p. 176°; 1-Me derivative picrate, m.p. 148—149°, obtained by reduction (H<sub>2</sub>, PtO<sub>2</sub>, EtOH) etc. of the methosulphate of (I)]. (II) with 40% CH<sub>2</sub>O and 2N-HCl at 100° affords 2':3':2'':3''-tetramethoxy-1:2:6:9-tetrahydro-3:4:7:8-dibenzquinolizine (III), decomp. 80° (becomes red) (methiodide, decomp. 197—198°). The unstable hydrochloride, decomp. ~180° (sinters and becomes red ~90°), of (III) is dehydrogenated by passing air through a solution in EtOH containing Pt-black; the product with KI in aq. HCl gives a (?) tetramethoxydibenzquinolizinium iodide, C<sub>21</sub>H<sub>20</sub>O<sub>4</sub>NI, m.p. 235°.

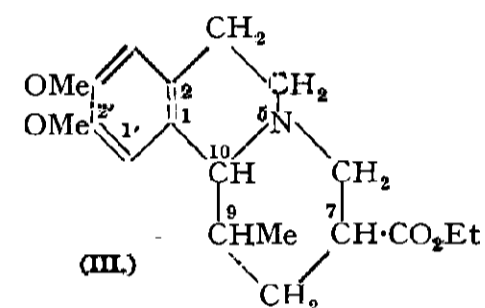
**XXII.** The generalisation previously made (A., 1939, II, 281) regarding the oxidation of 1-β-arylethylpyridinium salts to 1-β-arylethyl-2-pyridones is now found to be invalid. 2-Phenyl-4-3':4'-dimethoxy-6'-methylbenzylidene-5-oxazolone, m.p. 167—168.5° [from 3:4:6:1-(OMe)<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>Me·CHO, NHBz·CH<sub>2</sub>·CO<sub>2</sub>H, and Ac<sub>2</sub>O·NaOAc at 100°], is hydrolysed (10% NaOH in H<sub>2</sub>) to 3:4-dimethoxy-6-methylphenylpyruvic acid, m.p. 195—196.5°, which is oxidised (H<sub>2</sub>O<sub>2</sub>) to 6-methylhomoveratric acid, m.p. 102—104°, purified through its Et ester (IV), b.p. 162—164.5°/4 mm. Bouveault-Blanc reduction of (IV) gives 3:4:6:1-(OMe)<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>Me·[CH<sub>2</sub>]<sub>2</sub>·OH, b.p. 166—168°/4 mm. (*p*-nitrobenzoate, m.p. 114.5—116°), the bromide, b.p. 158—159°/4 mm. (prep. by PBr<sub>3</sub>), of which with C<sub>6</sub>H<sub>5</sub>N at 110° affords 1-β-3':4'-dimethoxy-6'-methylphenylpyridinium bromide, m.p. 154—156°. This is oxidised by aq. NaOH·K<sub>3</sub>Fe(CN)<sub>6</sub> to the non-cryst. 2-pyridone, which is converted by POCl<sub>3</sub> followed by aq. HCl-KI into 1':2'-dimethoxy-4'-methyl-3:4-dihydro-5:10-dehydro-1:2-benzquinolizinium iodide, decomp. 186.5—187° (becoming red) [the corresponding chloride readily absorbs 3 H<sub>2</sub> (PtO<sub>2</sub>-EtOH) to give a *tert*-base (hydriodide, m.p. 225—226°)]. *o*-Methoxybenzylidenerhodanine, decomp. 250° (from *o*-OMe·C<sub>6</sub>H<sub>4</sub>·CHO, rhodanine, and AcOH·NaOAc at 100°), with 15% NaOH gives *o*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CS·CO<sub>2</sub>H, m.p. 133—135°, converted by EtOH·NaOEt·NH<sub>2</sub>·OH·HCl into *o*-anisylpyruvic acid oxime (V), decomp. 162.5°. Crude (V) with Ac<sub>2</sub>O affords *o*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CN, new m.p. 71°, whence *o*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CO<sub>2</sub>Et, b.p. 135°/10 mm., and *o*-OMe·C<sub>6</sub>H<sub>4</sub>·[CH<sub>2</sub>]<sub>2</sub>·OH, b.p. 123—124°/8 mm. (*p*-nitrobenzoate, m.p. 59°). 1-β-*o*-Anisylethylpyridinium bromide (corresponding picrate, m.p. 114—115.5°) is oxidised to 1-β-*o*-anisylethyl-2-pyridone, m.p. 130—131°, 2:3:1-(OMe)<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·[CH<sub>2</sub>]<sub>2</sub>·OH, b.p. 125—128°/2 mm. (*p*-nitrobenzoate, m.p. 111—112°), gives the pyridinium bromide (corresponding picrate, m.p. 111—112°), converted (as above) into the 2-pyridone and thence into 3':4'-dimethoxy-3:4-dihydro-5:10-dehydro-1:2-benzquinolizinium iodide, decomp. 182° (corresponding picrate, m.p. 135—136°). Reduction (H<sub>2</sub>, PtO<sub>2</sub>, EtOH) of the chloride affords 3':4'-dimethoxy-3:4:6:7:8:9-hexahydro-1:2-benzquinolizine (picrate, m.p. 147.5°; hydriodide, m.p. 170°). 2:5-Dimethoxybenzylidenerhodanine, m.p. 243°, similarly yields 2:5-dimethoxyphenylpyruvic acid oxime, m.p. 153° (decomp.) (intermediate thio-acid, decomp. 186°), 2:5-dimethoxybenzyl cyanide, m.p. 54—55°, 2:5:1-(OMe)<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>Et, b.p. 162—165°/8 mm., 2:5:1-(OMe)<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·[CH<sub>2</sub>]<sub>2</sub>·OH, b.p. 161°/8 mm. (*p*-nitrobenzoate, m.p. 76—77.5°; bromide, b.p. 149—150°/8 mm.), the pyridinium

bromide, m.p. 53—54.5°, and picrate, m.p. 122°, the crude 2-pyridone, I' : 4'-dimethoxy-3 : 4-dihydro-5 : 10-dehydro-1 : 2-benzquinolizinium iodide, m.p. 156—157.5°, and chloride, m.p. 63°, and 1' : 4'-dimethoxy-3 : 4 : 6 : 7 : 8 : 9-hexahydro-1 : 2-benzquinolizine (picrate, m.p. 127—128.5°; methiodide, m.p. 158—159°).

$\beta$ -Nitro-2 : 5-dimethoxystyrene, m.p. 119—120.5° [from 2 : 5 : 1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CHO and MeNO<sub>2</sub> in EtOH-NH<sub>2</sub>Me], is reduced electrolytically in EtOH-AcOH-conc. HCl at a Pb cathode to 2 : 5 : 1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·[CH<sub>2</sub>]<sub>2</sub>·NH<sub>2</sub>. The Ac derivative, m.p. 98—99°, of this gives 5 : 8-dimethoxy-1-methyl-3 : 4-dihydroisoquinoline, b.p. 144—147°/2 mm., m.p. 67—68° (methiodide, m.p. 198—199°); catalytic reduction of the methochloride, m.p. 123—125°, affords 5 : 8-dimethoxy-1 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, b.p. 149—150°/5 mm. (picrate, m.p. 209—210°). The methosulphate of this with ~30% KOH at 100° gives  $\beta$ -2 : 5-dimethoxy-6-vinylphenylethyldimethylamine, b.p. 147—150°/10 mm. (picrate, m.p. 170—172°), reduced to the 6-Et derivative, b.p. 166—169°/25 mm. (picrate, m.p. 182—183°), which on further exhaustive methylation gives a product oxidised (KMnO<sub>4</sub>) to 3 : 6 : 1 : 2-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CO)<sub>2</sub>O.

H. B.

**Synthesis of nitrogen-containing heterocyclic rings. XXIII. Synthesis of ethyl 2' : 3'-dimethoxy-9-methyl-3 : 4 : 6 : 7 : 8 : 9-hexahydro-1 : 2-benzquinolizine-7-carboxylate.** S. Sugawara, K. Sakurai, and T. Okayama (*Ber.*, 1941, 74, [B], 537—541).—3-Carbomethoxy-, decomp. 197°, 3-carbethoxy-, decomp. 195°, and 3-carbamyl-, m.p. 209°, -1- $\beta$ -phenylethylpyridinium bromide (from Ph·[CH<sub>2</sub>]<sub>2</sub>·Br and the nicotinic acid derivative in xylene) are all oxidised by alkaline K<sub>2</sub>Fe(CN)<sub>6</sub> to 1- $\beta$ -phenylethyl-2-pyridone-5-carboxylic acid (I), m.p. 190°. Reduction (Na-Hg, H<sub>2</sub>O) of (I) gives 1- $\beta$ -phenylethyl-2-piperidone-5-carboxylic acid (II), m.p. 140—141°. Ph·[CH<sub>2</sub>]<sub>2</sub>·NH<sub>2</sub> and Et<sub>2</sub>  $\alpha$ -formylglutarate give a product which is reduced slowly by H<sub>2</sub>-PtO<sub>2</sub>-EtOH-AcOH to the Et ester of (II); Et<sub>2</sub>  $\alpha$ -formylsuccinate similarly gives the Et ester, b.p. 170—180°/4 mm., of 1- $\beta$ -phenylethyl-2-pyrrolidone-4-carboxylic acid, m.p. 192—193°. Et<sub>2</sub>  $\alpha$ -formyl- $\alpha'$ -methylglutarate, b.p. 108—113°/4 mm. (from CO<sub>2</sub>Et·[CH<sub>2</sub>]<sub>2</sub>·CHMe·CO<sub>2</sub>Et, HCO<sub>2</sub>Et, and Na in Et<sub>2</sub>O), with 3 : 4 : 1-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·[CH<sub>2</sub>]<sub>2</sub>·NH<sub>2</sub> similarly affords Et 1- $\beta$ -3' : 4'-



dimethoxyphenylethyl-3-methyl-2-piperidone-5-carboxylate, b.p. 208—215°/4 mm., converted by POCl<sub>3</sub> in boiling PhMe into 2' : 3'-dimethoxy-7-carbethoxy-9-methyl-3 : 4 : 6 : 7 : 8 : 9-hexahydro-5 : 10-dehydro-1 : 2-benzquinolizinium chloride, m.p. 177—178°, which is reduced (H<sub>2</sub>, PtO<sub>2</sub>, EtOH) to Et 2' : 3'-dimethoxy-9-methyl-3 : 4 : 6 : 7 : 8 : 9-hexahydro-1 : 2-benzquinolizine-7-carboxylate (III), m.p. 115—116° (possibly one of the r-forms).

H. B.

**Chemical constitution and antiplasmodic action. V. Derivatives of 2-chloro-5-amino-7-methoxyacridine.** V. Prelog, E. Rajner, and P. Stern (*Helv. Chim. Acta*, 1943, 26, 1172—1180).—The following are obtained from the  $\alpha$ -Br-ester and sec. amine (2 mols.) in C<sub>6</sub>H<sub>6</sub> at 100°: Et  $\alpha$ -diethylaminovalerate, b.p. 85°/15 mm. (reineckate, m.p. 123°); Et  $\alpha$ -dipropylaminobutyrate, b.p. 90°/16 mm. (picrate, m.p. 94°); Et  $\alpha$ -dibutylaminobutyrate, b.p. 133°/17 mm. (reineckate, m.p. 119°). Reduction (Bouveault-Blanc) of the appropriate NH<sub>2</sub>-ester gives the following:  $\beta$ -dipropylaminopropan- $\alpha$ -ol, b.p. 92°/12 mm. (reineckate, m.p. 128°);  $\beta$ -dipropylaminobutan- $\alpha$ -ol, b.p. 100°/16 mm. (hydrochloride, m.p. 121°);  $\beta$ -dibutylaminobutan- $\beta$ -ol, b.p. 125°/16 mm. (reineckate, m.p. 125°);  $\beta$ -diethylaminopentan- $\alpha$ -ol, b.p. 91°/16 mm. (reineckate, m.p. 127°). Treatment of the hydrochloride of the NH<sub>2</sub>-alcohol with SOCl<sub>2</sub> in CHCl<sub>3</sub> and of the resulting chloride with 18% NH<sub>3</sub>-MeOH at 100—120° leads to the following:  $\beta$ -diethylaminopropylamine, b.p. 67°/18 mm. (picrate, m.p. 127°), and di-( $\beta$ -diethylaminopropyl)amine, b.p. 150°/18 mm. (picrate, m.p. 132°);  $\beta$ -diethylamino-n-butylamine, b.p. 80°/20 mm. (picrate, m.p. 153—154°), and di-( $\beta$ -diethylaminobutyl)amine, b.p. 145°/20 mm. (picrate, m.p. 143°);  $\beta$ -diethylaminoamylamine, b.p. 84°/16 mm. (picrate, m.p. 163°);  $\beta$ -dipropylaminopropylamine, b.p. 89°/12 mm. (picrate, m.p. 187°), and di-( $\beta$ -dipropylaminopropyl)amine, b.p. 165°/12 mm. (picrate, m.p. 151°);  $\beta$ -dipropylaminobutylamine, b.p. 115°/18 mm. (picrate, m.p. 170°);  $\beta$ -dibutylaminobutylamine, b.p. 119°/16 mm. (picrate, m.p. 164°);  $\beta$ -piperidinopropylamine, b.p. 85°/25 mm. (picrate, m.p. 220°), and di-( $\beta$ -piperidinopropyl)amine, b.p. 175°/25 mm. (picrate, m.p. 169°);  $\beta$ -piperidinobutylamine, b.p. 94°/25 mm. (picrate, m.p. 198°);  $\alpha$ -aminomethylquinuclidine, b.p. 118°/14 mm. (picrate, m.p. 213°). Passage of NH<sub>3</sub> through 2 : 5-dichloro-7-methoxyacridine in PhOH at 170—180° gives 2-chloro-5-amino-7-methoxyacridine (I), m.p. 267° (lactate, m.p. 221—222°). Analogous methods lead to the following 2-chloro-7-methoxy-acridines: 5- $\alpha$ -quinuclidylmethylamino- (II), m.p. 157° (trihydrochloride, m.p. 282°); 5- $\beta$ -piperidinopropylamino-, m.p. 165°; 5- $\beta$ -piperidino-, butylamino-, m.p. 139°; 5- $\beta$ -diethylaminopropylamino-, m.p. 115° (trihydrochloride, m.p. 254°); 5- $\beta$ -diethylaminobutylamino- [trihydrochloride (+1H<sub>2</sub>O), m.p. 245.5°]; 5- $\beta$ -diethylaminoamylamino-, m.p. 112° (trihydrochloride, (+1H<sub>2</sub>O), m.p. 219—220°); 5- $\beta$ -dipropyl-

aminopropylamino-, m.p. 146° (dihydrochloride, m.p. 242°); 5- $\beta$ -dipropylaminobutylamino- [dihydrochloride (III), m.p. 240°]; 5- $\beta$ -dibutylaminobutylamino- [dihydrochloride (+1H<sub>2</sub>O), m.p. 218°]. (I) is devoid of antiplasmodic action. (II) and compounds with dialkylamino-groups in the side-chain are highly active; (III) is exceptional in being slightly toxic. Substances with a piperidine residue are inactive.

H. W.

**Polynuclear condensed systems with heterocyclic rings. VII. Ring-closure of 3-phenyl- and 3-benzyl-7 : 8-benzocinchonic acids.** W. Borsche and M. Wagner-Roemmich (*Annalen*, 1940, 544, 272—279; cf. A., 1937, II, 519; 1939, II, 348).—3-Phenyl-7 : 8-benzocinchonic acid, m.p. 282° (decomp.), is obtained from  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> (I), CH<sub>2</sub>Ph·CO·CO<sub>2</sub>H (II), and CH<sub>2</sub>O in hot aq. EtOH (22% yield) or from  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH·CHO (III) and (II) in EtOH at room temp. (42% yield) and, when melted with Cu-bronze, gives 3-phenyl-7 : 8-benzquinoline, m.p. 106—108°. (I) and (II) with MeCHO in hot EtOH or PhCHO in hot AcOH gives 3-phenyl-2-methyl-, m.p. 292° and 2 : 3-diphenyl-7 : 8-benzocinchonic acid, m.p. 271°, respectively, and thence 2 : 3-diphenyl-7 : 8-benzquinoline, m.p. 144°. Ph·[CH<sub>2</sub>]<sub>2</sub>·CO·CO<sub>2</sub>H (IV), (I), and PhCHO in EtOH give 2-phenyl-3-benzyl-7 : 8-benzocinchonic acid (V), m.p. 278° (decomp.), and thence 2-phenyl-3-benzyl-7 : 8-benzquinoline, m.p. 132—134°.  $\alpha$ -Naphth- isatin with COMe<sub>2</sub> and KOH in hot H<sub>2</sub>O-EtOH gives 2-methyl-, m.p. 238°, and with C<sub>6</sub>H<sub>5</sub>Me gives 2-phenyl-7 : 8-benzocinchonic acid, m.p. 288° (decomp.).  $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH·CHO with (II) or (IV) in hot EtOH gives 3-phenyl-, decomp. 293° (and thence 3-phenyl-5 : 6-benzquinoline), and 3-benzyl-5 : 6-benzocinchonic acid, m.p. 256°, respectively. Ring-closure of the cinchonic acids by conc. H<sub>2</sub>SO<sub>4</sub> at ~80° or by SOCl<sub>2</sub>-AlCl<sub>3</sub>-PhNO<sub>2</sub> gives naphtho-1' : 2'-2 : 1-3-azafluoren-9-one, m.p. 287° (oxime, m.p. 281°), and its 4-Me, m.p. 231° (oxime, m.p. 278°), and 4-Ph derivative, m.p. 267° (oxime, m.p. 269°), reduced by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O at 180—190° to naphtho-1' : 2'-2 : 1-3-azafluorene, m.p. 223°, and its 4-Me, m.p. 163°, and 4-Ph derivative, m.p. 189—190°, respectively. 3-Phenyl-2-benzyl-7 : 8-benzocinchonic acid could not be obtained, nor could (V) be cyclised.

R. S. C.

**Hydantoins.**—See B., 1943, II, 342.

**Barbituric acids.**—See B., 1943, III, 280.

**Many-membered cyclic compounds. XI. cycloDiocetamethylene-di-imine (1 : 10-diazacyclooctadecane).** A. Müller and L. Kindlmann (*Ber.*, 1941, 74, [B], 416—422).—Sebacamide is converted (Hofmann) into [CH<sub>2</sub>]<sub>8</sub>(NH<sub>2</sub>)<sub>2</sub> (I), the Bz<sub>2</sub> derivative, m.p. 173° (lit. 140°, 168.5°, 169.5°), of which with PBr<sub>3</sub> gives [CH<sub>2</sub>]<sub>8</sub>Br<sub>2</sub> (II), b.p. 140—142°/13 mm. (not obtained from Ag sebacate and Br). Very dil. solutions of (I) (as dihydrochloride), (II), and NaOH or Na<sub>2</sub>CO<sub>3</sub> in 50% EtOH containing ~0.5% of light petroleum and N<sub>2</sub> give 9—17% of cyclo-diocetamethylenedi-imine, m.p. 55° (sealed tube) [dihydrochloride, darkens ~365° without melting; (NO)<sub>2</sub>-derivative, m.p. 72°; aurichloride; platinichloride; picrate], when regenerated from its di-p-toluenesulphonyl derivative (III), m.p. 182°.  $\alpha\beta$ -Di-p-toluenesulphonamido-octane, m.p. 149°, and (II) added in successive portions to boiling C<sub>5</sub>H<sub>11</sub>·OH + K<sub>2</sub>CO<sub>3</sub> give 30% of (III). The base slowly absorbs CO<sub>2</sub> from the air. M.p. are corr.

H. B.

**Dipyrromethines.**—See B., 1943, II, 313.

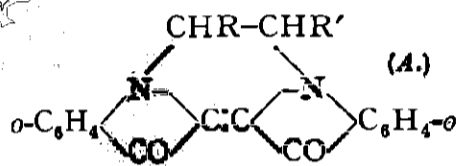
**Diopropyroquinone.** W. Siedel and F. Winkler (*Annalen*, 1943, 554, 201—212).—5-Hydroxy-2 : 4-dimethyl-3-ethylpyrrole is oxidised by Pb(OAc)<sub>4</sub> (2 mols.) in AcOH at 100° to an oil (I) from which 4-methyl-2-triacetoxymethyl-3-ethylpyrrolen-5-one (II), m.p. 124°, separates; it is not obtained when 3 mols. of the oxidant are used. (II) requires 4 mols. of NaOH for neutralisation but the pyrrolenone-carboxylic acid cannot be isolated; in its place, diopropyroquinone, CMe·C<sub>2</sub>Et>C:C<NH·CO  
CO-NH>C:C<C<sub>2</sub>Et·CMe (III), m.p. >300°, is formed in small amount. This is also obtained as by-product in the prep. of 5-methoxy-3-methyl-4-ethylpyrrole from 5-bromo-3-methyl-4-ethylpyrrole-2-carboxylic acid, its origin being due to the oxidation of an accompanying impurity, possibly 2 : 5-dihydroxyopropyrrole. (III) is stable towards H<sub>2</sub>O, acids, and alkalis, relatively stable towards heat. A quinuhydrone could not be produced. The yellow colour of (III) is discharged by addition of 1 mol. of H<sub>2</sub>, probably owing to destruction of conjugation by saturation of the linking joining the two nuclei. (III) is oxidised by HNO<sub>3</sub> to methyl-ethylmaleimide (IV). The portion of (I) which remains liquid consists mainly of (IV). Alkaline hydrolysis of (II) in presence of H<sub>2</sub>O<sub>2</sub> gives (IV). Cryptopyrryl formate, b.p. 135—150°/11 mm., gives only ill-defined oils when oxidised. Boiling MeOH-H<sub>2</sub>O (1 : 1) appears to convert (II) into 4-methyl-2-diacetoxymethyl-3-ethylpyrrolen-5-one, m.p. 150—156°, whilst KOH-MeOH gives 1-methoxy-4-methyl-2-dimethoxymethylene-3-ethylpyrrolen-5-one, sublimes at 220°.

R. S. C.

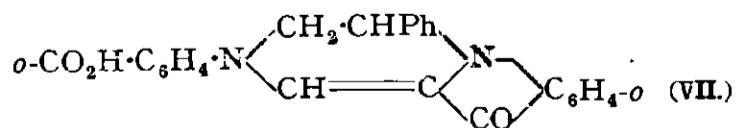
**Formation and properties of uretediones.** L. C. Raiford and H. B. Freyermuth (*J. Org. Chem.*, 1943, 8, 230—238).—Uretediones are obtained by adding PEt<sub>3</sub> to the liquid carbimide under N<sub>2</sub> at room temp., or by adding the catalyst to the molten carbimide or to a solution of it in dioxan. 1-p-Chlorophenyl-3-p'-tolyl-, m.p. 195°, 1 : 3-di-1'-naphthyl-, sublimes at 296°, and 1 : 3-di-2'-naphthyl-

uretedione, incipient decomp.  $\sim 220^\circ$ , are described. 1:3-Diphenyl-uretediones with substituents in Ph are obtained as follows, the yields being placed in parentheses: *di-3'-methyl-* (67), m.p. 159—160°; *di-4'-methyl-* (70), m.p. 185°; *di-4'-ethoxy-* (I) (95°), m.p. 181—182°; *di-2-chloro-* (37), m.p. 234—235°; *di-3'-chloro-* (72), m.p. 153—154°; *di-4'-chloro-*, (85), m.p. 155—156°; *di-4'-bromo-* (87), m.p. 203—204°; *di-4'-nitro-* (67), sublimes at 300°; *di-4'-phenyl-* (38), m.p. 270° (decomp.); *di-4'-benzeneazo-* (nearly quant.), m.p. 281—282° (decomp.). (I) is hydrolysed by boiling KOH-EtOH to  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2\cdot p$ . The biurets are usually obtained from the uretedione and two mol. proportions of the requisite amine in boiling EtOH.  $\alpha\gamma$ -Di-2'-naphthyl- $\epsilon$ -n-butylbiuret has m.p. 117—118°.  $\alpha\gamma$ -Diphenyl- $\epsilon$ -methyl-, m.p. 144—145°, - $\epsilon$ -ethyl-, m.p. 88—89°, - $\epsilon$ -n-propyl-, m.p. 115—116°, - $\epsilon$ -n-butyl-, m.p. 79—80°, - $\epsilon$ -iso-amyl-, m.p. 62—64°, - $\epsilon$ -allyl-, m.p. 94—95°, - $\epsilon\epsilon'$ -ethylene-, m.p. 171—172°, and  $\epsilon$ -piperidyl-biuret, m.p. 135—136°, are described.  $\alpha\gamma$ -Di-m-tolyl- $\epsilon$ -n-butyl-, m.p. 102—103°,  $\alpha\gamma$ -di-p-tolyl- $\epsilon$ -n-butyl-, m.p. 131—132°;  $\alpha\gamma$ -tri-p-tolyl-, m.p. 265°,  $\alpha\gamma$ -di-p-ethoxyphenyl- $\epsilon$ -methyl-, m.p. 110—111°,  $\alpha\gamma$ -di-m-chlorophenyl- $\epsilon$ -n-butyl-, m.p. 119—120°,  $\alpha\gamma$ -di-p-chlorophenyl- $\epsilon$ -n-butyl-, m.p. 104—105°, and  $\alpha\gamma$ -di-p-bromophenyl- $\epsilon$ -n-butyl-biuret, m.p. 118—120°, have been prepared. Successive treatments of  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$  in PhMe with dry HCl and  $\text{COCl}_2$  lead to  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph})_2$ , m.p. 270° (decomp.), and  $p$ -benzeneazo-phenylcarbimide, m.p. 94—95°. N-Phenyl-N'-n-butylcarbamide has m.p. 129—130°. H. W.

**Indigo dyes of the cis-series.** R. Pummerer and H. Fiesselmann [with O. Müller] (*Annalen*, 1940, 544, 206—239).—Dehydroindigo does not react with  $(\text{CH}\cdot\text{CO})_2\text{O}$  alone at the m.p. or in boiling  $\text{C}_6\text{H}_6$ ,  $\text{CH}_2\cdot\text{CH}\cdot\text{CN}$ ,  $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$ ,  $\text{CHCl}\cdot\text{CH}\cdot\text{OAc}$ ,  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CNS}$ , indene, dimethylfulvene, cyclopentadiene, or cyclohexene at 100°. It decomposes in boiling PhMe. It adds to styrene at 100° (exothermal; rising to 130—140°) to give a compound (A; R = Ph, R' = H) (I) (62%), m.p. 228—229°, with anethole + a little  $\text{C}_6\text{H}_6$  at room temp. or, better (84%), in boiling  $\text{C}_6\text{H}_6$  gives the compound (A; R =  $p\text{-C}_6\text{H}_4\cdot\text{OMe}$ , R' = Me) (II), m.p. 164—165°, with safrole + some  $\text{C}_6\text{H}_6$  at room temp. gives the compound (A; R = 3:4:1- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2$ , R' = H) (III), with isosafrole + some  $\text{C}_6\text{H}_6$  at the b.p. gives the compound (A; R = 3:4:1- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$ , R' = Me), and with isoeugenol Me ether at 100° gives the compound (A; R = 4:3:1- $\text{OH}\cdot\text{C}_6\text{H}_3\cdot\text{OMe}$ , R' = Me) (IV). The solid products are lighter than indigo; they are blue in alcohols, phenols, or AcOH, but dark red in  $\text{C}_6\text{H}_6$ , PhCl,  $\text{CCl}_4$ , or other non-polar solvents, except that (III) is blue in all solvents. Differences in colour are not due to association, since (I) is unimol. in PhOH or PhCl; it is probably not due to solvation, but to existence of two forms (cf. below); these two forms are not stereoisomerides since (A) are necessarily derived from *cis*-indigo, nor to the betaine form of Kuhn (*Naturwiss.*, 1932, 20, 618). (III) differs because the Ph is separated from the ring by  $\text{CH}_2$  and resembles rather *NN'*-diethylindigo. Structures are proved as follows. Conc.  $\text{HNO}_3$ -AcOH or  $\text{CrO}_3$ -AcOH oxidises (I) to "styrenedi-isatin" (V) (73%), m.p. 175° (*di-*

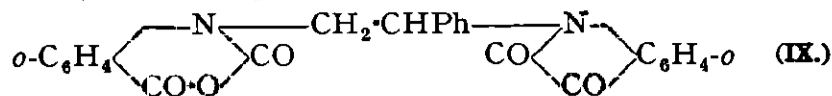


phenylhydrazone, m.p. 224°), which couples with hydroxythionaphthen to give the substance,  $\text{C}_{40}\text{H}_{24}\text{O}_4\text{N}_2\text{S}_2$ , m.p. 159—160° after sintering. (II) with  $\text{HNO}_3$ -AcOH gives similarly "anetholedi-isatin," m.p. 272—275°. With alkaline  $\text{H}_2\text{O}_2$  at 100° (V) gives "styrenedianthranilic acid,"  $\text{O}\cdot\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}\cdot\text{O}$  (VI) (89%), m.p. 214—215° (blue fluorescence in EtOH or  $\text{Et}_2\text{O}$ , not in  $\text{H}_2\text{SO}_4$ ), which in boiling  $\text{Ac}_2\text{O}$  gives 1-acetyl-2'-phenylindigotin (yellowish-green fluorescence in conc.  $\text{H}_2\text{SO}_4$ , not in  $\text{Et}_2\text{O}$  or EtOH; sol. in hot KOH-MeOH by enolisation). In boiling NaOH-, KOH-, or  $\text{Ba}(\text{OH})_2$ -EtOH, or slower, aq. NaOH, KOH,  $\text{Ba}(\text{OH})_2$ ,  $\text{Na}_2\text{CO}_3$ , or  $\text{Na}_2\text{HPO}_4$ , (I) gives "styreneindigo yellow" (VII) (85%), sinters at 205°, m.p. 210° [Ac derivative, m.p. 189° (decomp.)]. Similar dyes are obtained from (II), (III), and (IV) (product has m.p. 220—230°). (VII) is sol. in  $\text{NaHCO}_3$  etc., fluoresces in org. solvents, is yellow in conc.  $\text{H}_2\text{SO}_4$ , is readily and reversibly reduced by  $\text{Na}_2\text{S}_2\text{O}_4$  with disappearance of the fluorescence, and dyes wool greenish-yellow (not fast). It is probably formed by way of (VIII). Distilling (VII) with Zn dust gives indole and  $\text{NH}_2\text{Ph}$ .



Conc.  $\text{HNO}_3$ ,  $\text{CrO}_3$ , or  $\text{PbO}_2$  in AcOH, aq. alkaline  $\text{KMnO}_4$  or  $\text{K}_3\text{Fe}(\text{CN})_6$  converts (VII) into the compound (IX) (72—86%), m.p.

185—187° (2:4-dinitrophenylhydrazone), which neutralises 2 NaOH



rapidly and a third mol. slowly and with alkaline  $\text{H}_2\text{O}_2$  gives (VI).  $\text{H}_2\text{O}_2$  also converts (VII) or the "yellow" from (II) directly into (VI) and the compound,  $\text{C}_{26}\text{H}_{20}\text{O}_6\text{N}_2$ , respectively. R. S. C.

**Constitution of indigo [derivatives] as determined by absorption measurements.** G. Scheibe, H. Dörfling, and J. Assmann (*Annalen*, 1940, 544, 240—253).—The absorption spectra of the adducts of dehydroindigo with styrene or anethole (cf. preceding abstract) in  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ , *iso*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$ , EtOH, MeOH, and  $\text{NH}_2\text{Ph}$  differ only in the position of the max. and differ only in this way from that of indigotin in  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ , *iso*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$ , or  $\text{NH}_2\text{Ph}$ . The blue and red colours are not due to *cis-trans* isomerism since the adducts are *cis*-compounds. Distribution of the anethole adduct between aq. MeOH and  $\text{C}_6\text{H}_6$  or  $\text{CCl}_4$  precludes association in either solvent. Addition of *iso*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$  to the  $\text{CCl}_4$  solution causes changes in the absorption of the styrene adduct which are incompatible with the existence of different compounds in the two solvents. Variations in colour and absorption are thus due to mesomerism between (A; preceding

abstract) and perhaps the form,  $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}^+\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{N}^+\cdot\text{C}_6\text{H}_4\cdot\text{O}$ .

The safrole adduct and *NN'*-diethylindigo differ somewhat from the above compounds, but the causes are somewhat obscure. R. S. C.

**Condensation of chloral with 2-methyl-4-quinazolone, 2-methyl-3-amino-4-quinazolone, and some of their derivatives.** P. Y. Kulkarni (*J. Indian Chem. Soc.*, 1942, 19, 180—182).—2-Methyl-4-quinazolone and chloral (hot) yield 2- $\gamma\gamma\gamma$ -trichloro- $\beta$ -hydroxypropyl-, m.p. 204—205°, which with  $\text{Ac}_2\text{O}$  yields 2- $\gamma\gamma\gamma$ -trichloro- $\Delta^a$ -propenyl-4-quinazolone, m.p. 212°, and with 10% aq. NaOH at 60° gives 4-quinazolone-2-acrylic acid, m.p. 262—263°. Similarly 3-amino-4-quinazolone yields 3- $\beta\beta\beta$ -trichloro- $\alpha$ -hydroxyethylamino-, m.p. 151—152°, dehydrated (AcCl in  $\text{C}_5\text{H}_5\text{N}$ ) to 3- $\beta\beta\beta$ -trichloroethylideneamino-2-methyl-4-quinazolone, m.p. 104—105°. A. L. I.

**Polynuclear condensed systems with heterocyclic rings. VIII. Diazaphenanthrenecarboxylic acids and diazaphenanthrenes.** W. Borsche and M. Wagner-Roemmich (*Annalen*, 1940, 544, 280—286).—Aminoquinolines, RCHO, and  $\text{CH}_2\text{R}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  give sometimes diketopyrrolidines and sometimes diazaphenanthrenes. 3-Aminoquinoline, PhCHO, and  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  (I) in EtOH at 100° give 4:5-diketo-2:3-diphenyl-1:3'-quinolylpyrrolidine, m.p. 269—270°. 5-Aminoquinoline (II) (prep. from the  $\text{NO}_2$ -compound by  $\text{H}_2$ -Pd-C in AcOH), b.p. 183—187°/16 mm., with PhCHO and (I) or Ph- $[\text{CH}_2]_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$  (III) gives 4:5-diketo-2:3-diphenyl-, m.p. 186°, and -2-phenyl-3-benzyl- (picrate, m.p. 252°), -1:5'-quinolylpyrrolidine, respectively. 6-Aminoquinoline (IV) (prep. from  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  by a Skraup reaction and subsequent hydrogenation; >90% yield), m.p. 116°, b.p. 192—195°/14 mm., with MeCHO and (I) at the b.p. (2 days) gives mainly 4:5-diketo-3-phenyl-1:6'-quinolyl-2-methylpyrrolidine, m.p. 203°, and  $\sim 10\%$  of 3-phenyl-2-methyl-1:8-diazaphenanthrene-4-carboxylic acid, m.p. 288° (with loss of  $\text{CO}_2$  to yield 3-phenyl-2-methyl-1:8-diazaphenanthrene, m.p. 144°), but with PhCHO and (I) in AcOH at 100° or (III) in hot EtOH, (IV) gives 2:3-diphenyl- (V) (55%), m.p. 278°, and 2-phenyl-3-benzyl-1:8-diazaphenanthrene-4-carboxylic acid (good yield), m.p. 272°, respectively, decarboxylated by Cu-bronze at the m.p. to 2:3-diphenyl-, m.p. 242—243°, and 2-phenyl-3-benzyl-1:8-diazaphenanthrene, m.p. 98°, respectively. 8-Aminoquinoline, b.p. 150—154°/16 mm., is obtained from the 5- $\text{NO}_2$ -compound by  $\text{H}_2$ -Pd-C in AcOH or from 8-hydroxyquinoline and  $\text{CaCl}_2\cdot 8\text{NH}_3$  at 220—230° and later 280—290°, and with PhCHO and (I) gives 2:3-diphenyl-4:5-diazaphenanthrene-1-carboxylic acid, m.p. 260—262°. 5-Aminoisoquinoline with hot PhCHO and (I) gives, in 1—2 days, 2:3-diphenyl-4:7-diazaphenanthrene-1-carboxylic acid, m.p. 237°, and thence 2:3-diphenyl-4:7-diazaphenanthrene, m.p. 263—264°. When heated for 1 day with  $\text{SOCl}_2$  and then  $\text{AlCl}_3$  in  $\text{PhNO}_2$  at 50° or conc.  $\text{H}_2\text{SO}_4$  at 100°, (V) gives 4-phenylquinolino-5':6'-1:2:3-azafluoren-9-one, m.p. 242° (oxime, m.p. 213°), but ring-closure of the other acids could not be achieved. R. S. C.

**Polynuclear condensed systems with heterocyclic rings. IX. 7-Aminoquinolines and 1:5-diazaphenanthrene-4-carboxylic acids.** W. Borsche and M. Wagner-Roemmich (*Annalen*, 1940, 544, 287—300).— $m\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  (I) with  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  (II) and PhCHO in hot EtOH gives 7-hydroxy-2-n-propylcinchoninic acid, which at the m.p. (302°) gives  $\text{CO}_2$  and 7-hydroxy-2-n-propylquinoline (III), m.p. 132°. Use of other appropriate aldehydes gives 7-hydroxy-3-phenyl-2-methyl-, m.p. 323° (decomp.), 7-hydroxy-2:3-diphenyl- (20%), m.p. 313°, and 7-hydroxy-2-2'-furyl-cinchonic acid ( $\sim 50\%$ ), m.p. 311—312°, and thence 7-hydroxy-3-phenyl-2-methyl-, m.p. 258°, 7-hydroxy-2:3-diphenyl-, m.p. 277°, and 7-hydroxy-2-2'-furyl-quinoline, m.p. 265—266°. Ph- $[\text{CH}_2]_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$  (IV), (I), and MeCHO or PhCHO in hot EtOH give 7-hydroxy-3-benzyl-2-methyl- (50%), m.p. 307—

309° (decomp.), and 7-hydroxy-2-phenyl-3-benzyl-cinchonic acid, decomp. 327°, and thence 7-hydroxy-2-phenyl-3-benzylquinoline, m.p. 274°. With  $\text{CaCl}_2 \cdot 8\text{NH}_3$  (II) at 250° and then ~270° gives 7-amino-2-n-propylquinoline, m.p. 98° (picrate, m.p. 204°). 7-Hydroxy-2-phenylquinoline (acetate, m.p. 115°; benzoate, m.p. 123°; 8- $\text{PhN}_2$ -derivative, m.p. 197°; with  $\text{NaNO}_2$ -AcOH gives 2-phenylquinoline-7:8-quinone-8-oxime, m.p. 191°) with  $\text{CaCl}_2 \cdot 8\text{NH}_3$  at 250° and then 280—290° gives 7-amino-2-phenylquinoline (V) (~80%), m.p. 134° (picrate, m.p. 216°; Bz derivative, m.p. 222°; azo-dye, m.p. 233—234°, from 2:1-OH- $\text{C}_{10}\text{H}_6\text{N}_2\text{Cl}$ ); 7-hydroxy-gives similarly 7-amino-2-phenylcinchonic acid (hydrochloride, +2 $\text{H}_2\text{O}$ , m.p. ~166°), converted at the m.p. (274°) into  $\text{CO}_2$  and (IV). 2:4:1-( $\text{NO}_2$ ) $_2\text{C}_6\text{H}_3\text{CH}:\text{CH}:\text{CO}_2\text{H}$  (anilide, m.p. 222°) with  $\text{SOCl}_2$ - $\text{C}_6\text{H}_6$  and then  $\text{AlCl}_3$  at 40—50° gives 2:4-dinitrobenzylideneacetophenone, m.p. 151°, which with  $\text{SnCl}_2$ -HCl-AcOH gives exothermally the salt, (V),  $\text{SnCl}_2 \cdot \text{HCl}$ . With  $\text{PhCHO}$  and  $\text{AcCO}_2\text{H}$  at 100° (1 day), (V) gives 2:6-diphenyl-1:5-diazaphenanthrene-4-carboxylic acid, m.p. 268°, decarboxylated by Cu-bronze to give 2:6-diphenyl-1:5-diazaphenanthrene, m.p. 164° (picrate, m.p. 233—234°); use of (II) or (IV) gives 2:3:6-triphenyl-, m.p. 275° (decomp.), and 2:6-diphenyl-3-benzyl-1:5-diazaphenanthrene-4-carboxylic acid, m.p. 273° (decomp.), respectively, and thence 2:6-diphenyl-3-benzyl-1:5-diazaphenanthrene, m.p. 177°.  $m\text{-NH}_2\text{C}_6\text{H}_4\text{OMe}$  (modified prep.), b.p. 125—127°/13 mm., with  $\text{AcCO}_2\text{H}$ -paraldehyde or  $\text{-PhCHO}$  gives 7-methoxy-2-methyl-, m.p. 303°, and -2-phenyl-, m.p. 237—238°, respectively, with (II)-MeCHO or  $\text{-PhCHO}$  gives 7-methoxy-3-phenyl-2-methyl- (VI), m.p. 323°, and -2:3-diphenyl- (VII), m.p. 276—278°, and with (IV)- $\text{PhCHO}$ -EtOH gives 7-methoxy-2-phenyl-3-benzyl-cinchonic acid (VIII), m.p. 295°. Decarboxylation by Cu powder gives 7-methoxy-2-phenyl-, m.p. 127—128° (picrate, m.p. 186—187°), -2:3-diphenyl-, m.p. 149°, and -2-phenyl-3-benzyl-quinoline, m.p. 129°. Cyclisation of (VI) and (VII) by  $\text{COCl}_2$  and then  $\text{AlCl}_3$  in  $\text{PhNO}_2$  gives 9-keto-4-methyl-, m.p. 213° (oxime, m.p. 298°), and -4-phenyl-1:2:4'-methoxybenzo-3-azafluorene (~85%), m.p. 213°, but that of (VIII) failed.

R. S. C.

**New therapeutic agents of the quinoline series. I. Monopyridylquinolines.** H. Coates, A. H. Cook, I. M. Heilbron, D. H. Hey, A. Lambert, and (in part) F. B. Lewis. **II. Dipyridylquinolines.** A. H. Cook, I. M. Heilbron, D. H. Hey, A. Lambert, and (in part) A. Spinks. **III. Methoxy-, hydroxy-, and alkyl-pyridylquinolines.** H. Coates, A. H. Cook, I. M. Heilbron, D. H. Hey, A. Lambert, and (in part) F. B. Lewis. **IV. Lutidylquinolines.** A. H. Cook, I. M. Heilbron, and L. Steger. **V. Pyridylacridines.** A. H. Cook, I. M. Heilbron, and A. Spinks. **VI. Quinolyl-thiazoles, -amidines, and -pyrroles.** H. Coates, A. H. Cook, I. M. Heilbron, and F. B. Lewis (*J.C.S.*, 1943, 401—404, 404—406, 406—413, 413—417, 417—419, 419—420).—I. Existing spasmolytics are briefly reviewed, and their relation to the present series is indicated. The variation of anti-spasmodic action with changing orientation and substitution among pyridylquinolines and related compounds is described. Diazotised 3-aminoquinoline and  $\text{C}_5\text{H}_5\text{N}$  give a mixture from which can be separated, through the picrates, 3-2'-pyridylquinoline, m.p. 101.5° (picrate, m.p. 227—229°), and an isomeride, m.p. 123° [picrate, m.p. 196° (decomp.)]. 2-p-Aminophenylpyridine undergoes the Skraup reaction to a mixture of 5-, m.p. 88—89°, and 7-2'-pyridylquinolines, m.p. 87—88°. 2-p-Aminophenylpyridine is similarly converted into 6-2'-pyridylquinoline, m.p. 82—83°, whilst 6-3'-, m.p. 32—34° (dipicrate, m.p. 249—250°), and 6-4'-derivatives, m.p. 104—105°, are obtained from the corresponding  $\text{NH}_2$ -compounds. Addition of  $\text{C}_5\text{H}_5\text{N}$  to the diazotised base from the reduction of 8-nitroquinoline leads to a mixture of 8-2'-, m.p. 74—76° [picrate, m.p. 209—210°, styphnate, m.p. 181.5—182.5° (decomp.)], 8-3'-, m.p. 111—112° (picrate, m.p. 226°), and 8-4'-pyridylquinoline, m.p. 127° [picrate, m.p. 238—240° (decomp.)]. The constitution follows from the prep. of the 2'- and 3'-compounds from the 2- and 3-o-aminophenylpyridines by the Skraup reaction.

II. Nitration of 2-p-acetamidophenylpyridine gives the -3- $\text{NO}_2$ -compound, m.p. 142—143°, hydrolysed (NaOH) to 2-3'-nitro-4'-aminophenylpyridine, m.p. 148—149°. This undergoes the Skraup reaction to 8-nitro-6-2'-pyridylquinoline, m.p. 123—124°; reduced (Fe-HCl) to the 8- $\text{NH}_2$ -derivative, m.p. 125—126°, which after diazotisation and treatment with  $\text{C}_5\text{H}_5\text{N}$  gives 6-2'-pyridyl-8-2'-(3' and 4')-pyridylquinoline, m.p. 118—121°. 2-3':4'-Diaminophenylpyridine, m.p. 126—126.5°, by reduction of the  $\text{NO}_2$ -compound, with benzil gives 2:3-diphenyl-6-2'-pyridylquinoxaline, m.p. 198—199°. The diazotised mixture of 3-aminophenylpyridines with  $\text{C}_5\text{H}_5\text{N}$  affords 1:3-dipyridylbenzenes the dinitrate, m.p. 110—120°, of which with hot  $\text{H}_2\text{SO}_4$  gives 4-nitro-1:3-dipyridylbenzenes, m.p. 137—140°. This mixture after reduction undergoes the Skraup reaction ( $m\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ ) to 6:8-dipyridylquinolines, m.p. 152—156°. p-Aminophenylpyridine is converted similarly into dipyridylbenzene, which is nitrated to 2:5-dipyridylnitrobenzene. On reduction ( $\text{SnCl}_2$ -HCl), this affords 2:5-dipyridylaniline, converted (Skraup) into mixed 5:8-dipyridylquinolines, containing a fraction, m.p. 167°.

III. 2-3'-Amino-4'-methoxyphenylpyridine, m.p. 98° (Ac derivative, m.p. 171—172°), prepared from the corresponding  $\text{NO}_2$ -derivative, is converted (Skraup reaction) into 8-methoxy-5-2'-

pyridylquinoline, m.p. 115—116° [picrate, m.p. 196—198° (decomp.)]. 2-3'-Amino-6'-methoxyphenylpyridine (Ac derivative, m.p. 168—169°), similarly gives 6-methoxy-5(or 7)-, m.p. 100—101° (picrate, decomp. 222°), and -7(or 5)-2'-pyridylquinoline, m.p. 95° [picrate, m.p. 215—216° (decomp.)]. Diazotised 5-amino-6-methoxyquinoline with  $\text{NPhMe}_2$  affords a triazen,  $\text{C}_{12}\text{H}_{14}\text{ON}_4$ , m.p. 82—83°. Diazotised 8-amino-6-methoxyquinoline with  $\text{C}_5\text{H}_5\text{N}$  yields a mixture of 6-methoxy-8-2'- (I), m.p. 106—107° (picrate, m.p. 247—248°), -3'- (II), m.p. 100° (picrate, m.p. 243—244°), and -4'-pyridylquinoline, m.p. 146° [picrate, m.p. 260° (decomp.)]. Nitration ( $\text{HNO}_3$ -AcOH) and treatment with picric acid of 2-m-methoxyphenylpyridine gives in poor yield 2-2'-nitro-5'-methoxyphenylpyridine picrate, m.p. 190—191°, and two unidentified isomerides, m.p. 155—156°, and 273°. Diazotised 4-nitro-m-anisidine with  $\text{C}_5\text{H}_5\text{N}$  affords a mixture of 3-, m.p. 91—92° (picrate, m.p. 202—204°), and 2-2'-nitro-5'-methoxyphenylpyridine, m.p. 76°, which are reduced respectively to 3- (III), m.p. 131—132° (deaminated to 3-m-methoxyphenylpyridine picrate, m.p. 160—162°), and 2-2'-amino-5'-methoxyphenylpyridine (IV) (picrate, m.p. 193—194°). 4-m-Hydroxyphenylpyridine, m.p. 227—228°, is prepared by boiling the diazo-solution from the 4-m- $\text{NH}_2$ -compound. The Skraup reaction on (III) and (IV) gives (II) and (I) respectively, thus confirming the identities. o- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$  and 3-nitro-p-anisidine yield phthalo-3-nitro-p-aniside, m.p. 150°, reduced (Fe-HCl) to the -3- $\text{NH}_2$ -compound, m.p. 188°, the diazo-solution from which with  $\text{C}_5\text{H}_5\text{N}$  forms (IV), identified through the picrate. Nitration of (I) affords the 5- $\text{NO}_2$ -derivative, m.p. 192—193°, which is reduced (Fe-HCl) to the 5- $\text{NH}_2$ -compound, m.p. 124—125°. 2-, 3-, and 4-p-Aminophenylpyridine when heated with paraldehyde give respectively 6-2'-, m.p. 106—107°, -3'-, m.p. 65—66°, and -4'-pyridylquinaldine, m.p. 186°, whilst the 2'- and 3'-compounds with  $\text{AcCO}_2\text{H}$  afford 2-phenyl-6-2'-, m.p. 287—288° (decomp.), and -3'-pyridylquinoline-4-carboxylic acid, m.p. 301° (decomp.). Diazotised 2:1:4- $\text{NO}_2\text{C}_6\text{H}_3\text{Bu}^t\text{NH}_2$  with  $\text{C}_5\text{H}_5\text{N}$  forms a mixture of 3-nitro-4-tert-butylpyridylbenzenes, isolated as picrates A (3-?), m.p. 217—218°, B (4-?), m.p. 231° (decomp.), and C (2-?), m.p. 160°, from which the 3-(?) isomeride of the base has been liberated of b.p. 130°/high vac. Diazotised 3:1:4- $\text{NO}_2\text{C}_6\text{H}_3\text{Bu}^t\text{NH}_2$  with  $\text{C}_5\text{H}_5\text{N}$  gives 2-nitro-4-tert-butylpyridylbenzene, b.p. 170—190°/0.05 mm., reduced ( $\text{SnCl}_2$ -HCl) to the 2- $\text{NH}_2$ -compound, b.p. 136—141°/0.02 mm., which undergoes the Skraup reaction to 8-pyridyl-5-tert-butylquinoline, b.p. 120°/high vac. 2-3'-Nitro-4'-aminophenylpyridine boiled with KOH gives the -4-OH-compound, m.p. 125°, reduced to the 2-3'-amino-4'-hydroxy-derivative, m.p. 166—167°. This compound undergoes the Skraup reaction to form 8-hydroxy-5-2'-pyridylquinoline, m.p. 133.5—134°, which with  $\text{CH}_2\text{N}_2$  affords a substance, m.p. >250°. Nitration of 3-p-acetamidophenylpyridine leads to the -3- $\text{NO}_2$ -derivative, m.p. 169° (decomp.), hydrolysed (KOH) to 3-3'-nitro-4'-aminophenylpyridine, m.p. 176—177°. Reduction ( $\text{PtO}_2$ - $\text{H}_2$ ) of this compound gives 3-3':4'-diaminophenylpyridine, m.p. 122—123°, which with glyoxal forms 6-3'-pyridylquinoxaline, m.p. 144—145°, with benzil yields 6-3'-pyridyl-2:3-diphenylquinoxaline, m.p. 194.5—196.5°, and with isatin forms two products,  $\text{C}_{19}\text{H}_{12}\text{N}_4$ , m.p. 275—276°, and 307—308° (decomp.). The appropriate pyridylaniline with  $\text{CH}_2\text{AcCO}_2\text{Et}$  affords 3-, m.p. 154.5°, and 4-4'-pyridylacetoacetanilide, m.p. 136°, which, after heating and successive treatments with HCl and aq.  $\text{NH}_3$  gives s-bis-2-4'-pyridylphenylcarbamide, m.p. 278° (decomp.).

IV. Quinoline-2-aldehyde with  $\text{NH}_2\text{CMe}:\text{CH}:\text{CO}_2\text{Et}$  gives Et 4-2'-quinolyl-2:6-dimethyldihydropyridine-3:5-dicarboxylate, m.p. 190°, converted by  $\text{HNO}_3$  into the -dimethylpyridine-3:5-dicarboxylate, m.p. 91°, of which the Ag salt affords on heating 2-lutidylquinoline, m.p. 135° [picrate, m.p. 230° (decomp.)]. Quinoline-3-carboxylic ester and  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  yield quinoline-3-carboxyhydrazide, m.p. 190°, converted through the p-toluenesulphonyl derivative, m.p. 232° (decomp.), into quinoline-3-aldehyde, m.p. 70°. With  $\text{CH}_2\text{AcCO}_2\text{Et}$ , this aldehyde gives Et 4-3'-quinolyl-2:6-dimethyldihydro-, m.p. 193°, converted similarly into the -dimethylpyridine-3:5-dicarboxylate, m.p. 77°, and 3-lutidylquinoline, m.p. 100°. Quinoline-4-aldehyde similarly yields Et 4-4'-quinolyl-2:6-dimethyldihydro-, m.p. 200°, -dimethylpyridine-3:5-dicarboxylate, m.p. 122°, and 4-lutidylquinoline, m.p. 122°. Et quinoline-5-carboxylate, b.p. 190—192°/15 mm., m.p. 10°, from the corresponding acid, is converted through the p-toluenesulphonyl derivative of the hydrazide, m.p. 200°, into quinoline-5-aldehyde, m.p. 96°. This undergoes the same reactions to give Et 4-5'-quinolyl-2:6-dimethyldihydro-, m.p. 201°, -dimethylpyridine-3:5-dicarboxylate, m.p. 79°, and 5-2':6-lutidylquinoline, m.p. 151° (picrate, m.p. 231—234°). Et 4-p-nitrophenyl-2:6-dimethylpyridine-3:5-dicarboxylate, m.p. 115°, from the corresponding  $\text{H}_2$ -ester, is reduced ( $\text{Sn}$ -HCl) to the - $\text{NH}_2$ -ester, m.p. 145°, from which the free acid is decarboxylated to 4-p-amino-phenyl-2:6-dimethylpyridine, m.p. 131°, converted (Skraup) into 6-lutidylquinoline (V), m.p. 84° (picrate, m.p. 224—225°). Et quinoline-6-carboxylate is converted through the p-toluenesulphonyl derivative of the hydrazide, m.p. 218° (decomp.), into quinoline-6-aldehyde, which forms successively Et 4-6'-quinolyl-2:6-dimethyldihydro-, m.p. 209°, -dimethylpyridine-3:5-dicarboxylate, m.p. 97°, and (V). 5-Acetamidoquinoline, through its  $\text{NO}$ -derivative, with 2:6-lutidine affords a mixture from which can be separated 6-3'-2':6'-dimethylpyridylquinoline, m.p. 68° [picrate, m.p. ~243°

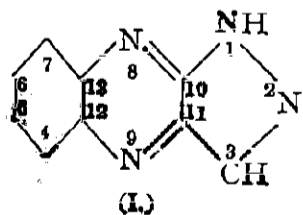
(decomp.)). *m*-Aminophenyl-lutidine, m.p. 117° (lit. 110°), by the Skraup reaction forms a mixture of 7-, m.p. 125° (picrate, m.p. 223°), and 5-lutidylquinoline, m.p. 151° (picrate, m.p. 231—234°). *Et* quinoline-8-carboxylate, b.p. 194—197°/13 mm., from the acid, affords successively quinoline-8-carboxyhydrazide, m.p. 99°, and its *p*-toluenesulphonyl derivative, m.p. 187°, quinoline-8-aldehyde, *Et*<sub>2</sub> 4-8'-quinolyl-2:6-dimethyldihydro-, m.p. 161°, and -dimethylpyridine-3:5-dicarboxylate, m.p. 80°, and 8-lutidylquinoline, m.p. 132°.

V. 2-*p*-Aminophenylpyridine with *o*-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H, K<sub>2</sub>CO<sub>3</sub>, and Cu in C<sub>5</sub>H<sub>11</sub>·OH gives 4-2''-pyridyldiphenylamine-2'-carboxylic acid (V), m.p. 198°, cyclised (H<sub>2</sub>SO<sub>4</sub>) to 3-2'-pyridylacridone, m.p. 315—317°, which is reduced (EtOH-Al-Hg) to the -acridine, m.p. 140°. A similar series of reactions affords 4-3'', m.p. 248—250°, and 4-4''-pyridyldiphenylamine-2'-carboxylic acid, m.p. 244°, 3-3'', m.p. 314—316°, and 3-4'-pyridylacridone, m.p. 343°, and 3-3', m.p. 132°, and 3-4'-pyridylacridine, m.p. 179°. 2-2''-Pyridyldiphenylamine-2'-carboxylic acid, m.p. 165—166°, yields successively 1-2'-pyridyl-acridone, m.p. 186—187°, and -acridine, m.p. 111.5°. Nicotinic acid and NHPb<sub>2</sub> with ZnCl<sub>2</sub> afford 5-3'-pyridylacridine, m.p. 118°. Diazotised NHPb·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>·*p* with C<sub>5</sub>H<sub>5</sub>N gives only one, 4-2''-pyridyldiphenylamine, m.p. 133° (picrate, m.p. 196.5°), also obtained by decarboxylation of (V).

VI. 2-Cyanoquinoline with aq. NH<sub>3</sub> and H<sub>2</sub>S gives quinoline-2-thioamide, m.p. 168—169°, which with CH<sub>2</sub>Br·COMe affords 2-5'-methyl-2'-thiazylquinoline, m.p. 121.5—122.5°. Similarly, quinoline-3, m.p. 197—198° (decomp.), -4-, m.p. 223° (decomp.), -5-, m.p. 187—188° (decomp.), -6-, m.p. 184—185° (decomp.), and -8-thioamide, m.p. 112—112.5° (decomp.), and 3-5', m.p. 118—118.5°, 4-5', m.p. 82.5—83.5°, 5-5', m.p. 97—98°, and 6-5'-methyl-2'-thiazyl-, m.p. 90.5—91.5°, and 8-2'-thiazylquinoline, m.p. 69—70°. Quinoline-2- [picrate, m.p. 258—259° (decomp.)], -3- [hydrochloride, m.p. 168—169° (decomp.)], and -6-amidine [hydrochloride, m.p. 242° (decomp.)] are prepared from the corresponding cyanoquinolines. The appropriate aminoquinolines with Et diacetylsuccinate in AcOH-EtOH afford *Et* 1-5'-quinolyl-, m.p. 99°, -6'-quinolyl-, m.p. 115°, -6'-methoxy-8'-quinolyl-, m.p. 141°, and -8'-methoxy-6'-quinolyl-2:5-dimethylpyrrole-3:4-dicarboxylate, m.p. 117°, and with (CH<sub>3</sub>Ac)<sub>2</sub> yield 1-3'-quinolyl-, m.p. 167°, and 1-6'-methoxy-8'-quinolyl-2:5-dimethylpyrrole, m.p. 147°. F. R. S.

3:6-Diazacarbazole. E. Koenigs and P. L. Nantka (*Ber.*, 1941, 74, [B], 215—217).—As 4-chloro-3-nitropyridine fails to undergo the Wurtz-Fittig reaction, 2:7-diazacarbazole was not accessible from the anticipated 3:3'-dinitro-4:4'-dipyridyl. When 4'-pyridyl-3:4-pyridotriazole (I) (*A.*, 1933, 720) is added to paraffin oil at 280—290° (or syrupy H<sub>2</sub>PO<sub>4</sub>) and the mixture heated at 320°, the diacid base, 3:6-diazacarbazole (II), m.p. 328° (dinitrate, m.p. 275—276°; picrate, m.p. 310°; methochloride, m.p. 259—260°), is obtained in 60% yield. (II) does not give carbazole colour reactions and is inert towards Br, HNO<sub>3</sub>, and NaNH<sub>2</sub> but adds Me<sub>2</sub>SO<sub>4</sub> readily. Similarly, the 3'-NH<sub>2</sub>-derivative of (I) affords 1-amino-3:6-diazacarbazole, m.p. >350° (nitrate, m.p. >350°; picrate, m.p. 283°), which can be diazotised and coupled with *α*-C<sub>10</sub>H<sub>7</sub>·OH to give a bluish-red colour J. Wa.

Flavazole, a new heterocyclic system from sugars. I. 1-Phenyl-3-(*d*-erythrotrihydroxypropyl)flavazole. Constitution of the side-chain. H. Ohle and G. A. Melkonian (*Ber.*, 1941, 74, [B], 279—291; cf. *A.*, 1943, II, 309).—Pyrazolo-3':4'-2:3-quinoxaline (I) is called "flavazole" and is numbered as shown. The substance C<sub>18</sub>H<sub>15</sub>O<sub>3</sub>N<sub>4</sub> (II), obtained by the action of NHPb·NH<sub>2</sub> and boiling dil. AcOH on 3-*d*-arabotetrahydroxybutylquinoxaline, is shown to be 1-phenyl-3-(*d*-erythrotrihydroxypropyl)flavazole and the mechanism of its formation is discussed. (II) (improved prep.), CPh<sub>3</sub>Cl, and C<sub>5</sub>H<sub>5</sub>N give 1-phenyl-3-(3'-tri-

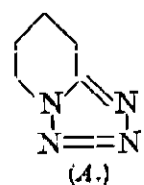


phenylmethyl-*d*-erythrotrihydroxypropyl)flavazole, m.p. 108—110° after regeneration from the diacetate, m.p. 163.5°, [α]<sub>D</sub><sup>20</sup> +65.7° in CHCl<sub>3</sub>. (II), COMe<sub>2</sub>, and H<sub>2</sub>SO<sub>4</sub> afford 1-phenyl-3-(2':3'-isopropylidene-*d*-erythrotrihydroxypropyl)flavazole (III), m.p. 147°, [α]<sub>D</sub><sup>18</sup> +1.3° in CHCl<sub>3</sub>. Benzoylation of (III) in C<sub>5</sub>H<sub>5</sub>N affords the 1'-Bz derivative (IV) of (III), m.p. 132—133°, [α]<sub>D</sub><sup>20</sup> -35.4° in CHCl<sub>3</sub>, and the isomeric 1-phenyl-3-(3'-benzoyl-1':2'-isopropylidene-*d*-erythrotrihydroxypropyl)flavazole (V), m.p. 161°, [α]<sub>D</sub><sup>25</sup> +22.3° in CHCl<sub>3</sub>. (IV), hydrolysed with AcOH, gives 1-phenyl-3-(1'-benzoyl-*d*-erythrotrihydroxypropyl)flavazole (VI), two forms, m.p. 183—184° and 175—177°, [α]<sub>D</sub><sup>21</sup> +11.48° and ~+3° respectively; acyl migration is suspected to be the cause, but both forms regenerate (V) with COMe<sub>2</sub>. The 1':2':3'-Bz<sub>3</sub> derivative of (II) has m.p. 155—155.5°, [α]<sub>D</sub><sup>18</sup> -74.2° in CHCl<sub>3</sub>. (II), BzCl, and C<sub>5</sub>H<sub>5</sub>N afford the 3'-Bz derivative (VII), m.p. 185—186°, [α]<sub>D</sub><sup>20</sup> ~-50° in C<sub>5</sub>H<sub>5</sub>N, and one other homogeneous substance, C<sub>32</sub>H<sub>24</sub>O<sub>5</sub>N<sub>4</sub>, presumably a dibenzoate, m.p. 159°. (VII) condenses with COMe<sub>2</sub> to give (V), which is hydrolysed (Zemplén) to 1-phenyl-3-(1':2'-isopropylidene-*d*-erythrotrihydroxypropyl)flavazole, m.p. 200—201°. (VI) with Pb(OAc)<sub>4</sub> in C<sub>5</sub>H<sub>6</sub> gives 60% of the theoretical CH<sub>2</sub>O and 65% of (1-phenyl-3-flavazolyl)-O-benzoylglycollaldehyde, m.p. 147°, [α]<sub>D</sub><sup>20</sup> +101.1° in CHCl<sub>3</sub> [unstable phenylhydrazone, m.p. 124—125° (decomp.)], and 2-phenyl-3-flavazolylmethylosazone, m.p. 110.5—

111°, [α]<sub>D</sub><sup>26</sup> -152.1° in CHCl<sub>3</sub>; unstable 2:4-dinitrophenylhydrazone, m.p. 230° (decomp.); dihydrophenylmethylosazone, m.p. 162—163°. (VII) and Pb(OAc)<sub>4</sub> afford 1-phenylflavazole-3-aldehyde (VIII), m.p. 144° (red "phenylhydrazone," m.p. 196—197°, converted by acid into a violet-red form, m.p. 223°; 2:4-dinitrophenylhydrazone, m.p. 271—272°), and OBz·CH<sub>2</sub>·CHO, isolated as the 2:4-dinitrophenylhydrazone, m.p. 185° (cf. *A.*, 1943, II, 350). (VIII) may be obtained by direct Pb(OAc)<sub>4</sub> oxidation of (II). J. Wa.

Flavazole. II. Structure of the ring system. H. Ohle and G. A. Melkonian (*Ber.*, 1941, 74, [B], 398—408).—Oxidation (CrO<sub>3</sub> in boiling AcOH) of 1-phenyl-3-*αβ*-trihydroxypropylflavazole (I) or the 3-CHO derivative (preceding abstract) gives 65—70% of 1-phenylflavazole-3-carboxylic acid (II), m.p. 244° (decomp.) (*Et* ester, m.p. 168°), decarboxylated at 260° (bath)/vac. to 1-phenylflavazole (III), m.p. 152.5—153.5°. 4:5-Diketo-1-phenyl-4:5-dihydropyrazole, an oil [from 1-phenyl-5-pyrazolone and *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub> (IV) in aq. EtOH-Na<sub>2</sub>CO<sub>3</sub> and subsequent hydrolysis (dil. H<sub>2</sub>SO<sub>4</sub> + Et<sub>2</sub>O)], and *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> in aq. EtOH-AcOH afford the 4-*o*-aminoanilo-derivative, m.p. 274° (decomp.), converted by boiling N-NaOH into (III) (poor yield). The flavazole structure of (I) is thus confirmed. Contrary to Sachs *et al.* (*A.*, 1902, i, 503), 4:5-diketo-1-phenyl-3-methyl-4:5-dihydropyrazole similarly gives the 4-*o*-aminoanilo-derivative (V) (+EtOH), and EtOH-free, both forms, m.p. 223° (decomp.), and not 1-phenyl-3-methylflavazole (VI), m.p. 133.5—134°. (VI) is obtained from (V) by boiling AcOH (36 hr.) or N-NaOH (~1 min.). (VI) does not react with PhCHO, is not attacked appreciably by SeO<sub>2</sub>, and with Br-AcOH at 100° gives an additive compound [regenerates (VI) with cold EtOH]; the Me could not be oxidised (KMnO<sub>4</sub>, CrO<sub>3</sub>) to CO<sub>2</sub>H. With CrO<sub>2</sub>Cl<sub>2</sub>-CS<sub>2</sub>, (VI) affords di-(*αβ*-di-1-phenyl-3-flavazolylethyl) ether, m.p. 356—358°. Attempts to synthesise 4:5-diketo-1-phenyl-4:5-dihydropyrazole-3-carboxylic acid [as an intermediate for the prep. of (II)] were unsuccessful. Et 5-keto-1-phenyl-4:5-dihydropyrazole-3-carboxylate (VII), new m.p. 181.5—182.5°, and NaNO<sub>2</sub> in 3-5N-KOH added to an excess of cold dil. HCl give the 4-oximino-ester, m.p. 171—172° (decomp.), from which :N·OH could not be removed; with *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> and H<sub>3</sub>BO<sub>3</sub> in dil. AcOH and CO<sub>2</sub> at 100° an adduct, C<sub>18</sub>H<sub>15</sub>O<sub>3</sub>N<sub>5</sub>, m.p. 260°, results. With (IV) in EtOH, (VII) affords (mainly) Et<sub>2</sub> 5:5'-dihydroxy-1:1'-diphenyl-4:4'-dipyrazolyl-3:3'-dicarboxylate (VIII), m.p. 273° (decomp.) (discoloured at 263°) (diacetate, m.p. 169°) [the leucopyrazole-blue of Ruhemann (*J.C.S.*, 1896, 69, 1396)], and a little of the dye (A) (R = CO<sub>2</sub>Et). With SeO<sub>2</sub>-EtOH, (VII) gives (VIII). 4-Oximino-5-keto-1-phenyl-4:5-dihydropyrazole-3-carboxylic acid, m.p. (solvent-free) 209° (also +0.5 EtOH or *α*MeOH) (Chattaway *et al.*, *A.*, 1927, 1087), with EtOH-*o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> affords a salt, C<sub>16</sub>H<sub>15</sub>O<sub>4</sub>N<sub>5</sub>, m.p. 161° (decomp.), but in aq. AcOH-H<sub>3</sub>BO<sub>3</sub> gives an adduct, C<sub>18</sub>H<sub>15</sub>O<sub>4</sub>N<sub>5</sub>, m.p. 260—265° (decomp.). Oxidation of 1-phenyl-3-methyl-5-pyrazolone with SeO<sub>2</sub> in EtOH or AcOH affords 5:5'-dihydroxy-1:1'-diphenyl-3:3'-dimethyl-4:4'-dipyrazolyl, m.p. ~320°, or the dye (A) (R = Me), m.p. 242—244° (decomp.), respectively. Et 5-keto-1-phenyl-4:5-dihydropyrazole-4-carboxylate has m.p. 104° (from petroleum) or 118—119° [from EtOH-NaOH (trace)]. H. B.

Syntheses in the tetrazole series. II. J. von Braun and W. Rudolph (in part with R. Michaelis) (*Ber.*, 1941, 74, [B], 264—272; cf. *A.*, 1933, 76).—CPhCl·NPh in CHCl<sub>3</sub> with 10% HN<sub>3</sub> in CHCl<sub>3</sub> gives ~100% of 1:5-diphenyltetrazole (I). Analogously prepared are: 1-phenyl-5-*p*-tolyl-, m.p. 136°; 5-phenyl-1-*p*-tolyl-, m.p. 132°; 1:5-di-*p*-tolyl-, m.p. 148°; 1-phenyl-5-*o*-tolyl-, impure; 1:5-di-*o*-tolyl-, impure; 1-phenyl-5-*o*-, m.p. 168°, -5-m-, m.p. 156°, and -5-*p*-nitrophenyl-, m.p. 178°; 5-phenyl-1-*o*-, m.p. 168°, and 1-*m*-nitro-, m.p. 133°; 1:5-di-*p*-(II), m.p. 262°, 1:5-di-*m*-, m.p. 244°, 1:5-di-*o*-nitrophenyl-, m.p. 209°; 1-*m*-nitrophenyl-5-*p*-nitrophenyl; 1-phenyl-5-(2':4'-, m.p. 164°, and -(3':5'-dinitro)phenyl-, m.p. 208°; 5-phenyl-1-methyl-tetrazole (III), b.p. 144—146°/0.3 mm., m.p. 102—103°. NHBu<sup>o</sup>Bz, b.p. 186—190°/12 mm., is converted via CPhCl·NBu<sup>o</sup>, b.p. 105°/high vac., into 5-phenyl-1-butyltetrazole (IV), b.p. 190—193°/12 mm. Benz-*n*-octylamide, m.p. 49°, is converted via *n*-C<sub>8</sub>H<sub>17</sub>·N·CPhCl, b.p. 170°/12 mm., into 5-phenyl-1-*n*-octyltetrazole, b.p. 205°/0.5 mm. *n*-C<sub>17</sub>H<sub>35</sub>·COPh (from C<sub>17</sub>H<sub>35</sub>·COCl, C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub>) is reduced (Clemmensen) to *n*-C<sub>18</sub>H<sub>37</sub>Ph, m.p. 29°, nitrated to *p*-*n*-C<sub>18</sub>H<sub>37</sub>·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>, b.p. 250—252°/0.5 mm., which is reduced to *p*-octadecylaniline, b.p. 240—245°/0.4 mm., and the Bz derivative, m.p. 118°, is converted into 5-phenyl-1-*p*-octadecylphenyltetrazole (V), m.p. 80°. 2-Chloropyridine and 2-chloroquinoline and HN<sub>3</sub> (not NaN<sub>3</sub>) give respectively "1:5-isobenzotetrazole" (A), m.p. 159°, and "1:5-iso-*α*-naphthotetrazole," m.p. 157°. (III) does not react with AcCl, AlCl<sub>3</sub>, CH<sub>2</sub>O-HCl, or Br; (I) does not react with Br even at 130—140°. 5-*p*-Tolyl-1-methyltetrazole, m.p. 113° (obtained from *p*-C<sub>6</sub>H<sub>4</sub>Me·CO·NHMe, m.p. 138°, b.p. 160°/0.5 mm., via *p*-C<sub>6</sub>H<sub>4</sub>Me·CCl·NMe, b.p. 114°/14 mm.), reacts with Br; the Br-derivative is not obtained pure but reacts with NH<sub>2</sub>Et<sub>2</sub> to give the NEt<sub>2</sub>-derivative, C<sub>12</sub>H<sub>19</sub>N<sub>5</sub>, m.p. 109° (oily picrate; hydrochloride, m.p. 135°), which reverts to the Br-derivative with BrCN.



Me groups in tolyltetrazoles are oxidised ( $\text{CrO}_3$  in  $\text{AcOH}$ ) with difficulty; 1-phenyl-5-p-carboxyphenyl- (?), m.p.  $267^\circ$  (chloride, m.p.  $104^\circ$ ), and 1 : 5-di-p-carboxyphenyl-tetrazole, m.p.  $310^\circ$  (chloride, m.p.  $174^\circ$ ), have been isolated. Aromatic substituted tetrazoles are very stable towards  $\text{HNO}_3$  but (IV) gives a p(?) - $\text{NO}_2$ -derivative, b.p.  $205^\circ/0.5$  mm., and, under vigorous conditions, (I) gives (II), m.p.  $260^\circ$ . Sulphonation introduces one  $\text{SO}_3\text{H}$  group into (I), the Na salt giving the anilide (VI), m.p.  $213^\circ$ . Reference compounds were synthesised as follows: p- $\text{SO}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ , b.p.  $150^\circ/12$  mm., m.p.  $57^\circ$ , gives the dianilide, m.p.  $251^\circ$ , and then 1-phenyl-5-p-sulphonanilidophenyl-tetrazole (VII), m.p.  $180^\circ$ , mixed m.p. with (VI)  $162\text{--}170^\circ$ ; m-sulphobenzdianilide, m.p.  $166^\circ$ , affords the m-isomeride, m.p.  $\sim 136^\circ$ , of (VII); p-NHBz $\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ , m.p.  $176^\circ$ , is converted through the anilide, m.p.  $223^\circ$ , into (VI), m.p. and mixed m.p.  $213^\circ$ . (IV) and (V) also undergo sulphonation and aq. solutions of the Na salts have foaming properties. J. WA.

**Tetrazole.**—See B., 1943, III, 280.

**Wing-pigments of butterflies. VI. Leucopterin and xanthopterin.** H. Wieland and R. Purrmann. **VII. Synthesis of leucopterin. Nature of guanopter.** R. Purrmann (*Annalen*, 1940, 544, 163—182, 182—190; cf. A., 1940, II, 236).—VI. Numerous analyses show leucopterin (I) to be  $(\text{C}_8\text{H}_5\text{O}_3\text{N}_5)_x$  and xanthopter (II)  $(\text{C}_8\text{H}_5\text{O}_2\text{N}_5)_x$  ( $x = 1$  or  $2$ ); many derivatives are similarly revised. "Iminoleucopterin" (A., 1939, II, 392) is really (I) (X-ray spectra). It is best (63%) obtained by shaking Ba xanthopter with  $\text{O}_2$  and Pt in aq.  $\text{NaOH}\text{--}\text{Na}_2\text{CO}_3$  (not 2N-HCl). Evaporating leucopterin glycol with 0.1N-LiCl (4 mols.) at room temp. (desiccator) gives 2-imino-5-hydantoinyl-oxamic acid (III) (58%) and -oxamide (IV) (20%) (*loc. cit.*); titrating with 0.1N-LiOH and evaporating at  $100^\circ$  gives (IV) (69%) and (III) (15%); titrating (IV) with 0.1N-LiOH and evaporating at room temp. gives (III) (50%). In 25% HCl at  $75^\circ$  (IV) gives 5-amino-2-iminohydantoin (64%) (dihydrochloride), which with KCNO in faintly acid solution gives 2-iminoallantoin (88%). Alkaline  $\text{H}_2\text{O}_2$  converts (II) or di-iminouric acid into imino-oxonic acid,  $\text{NH}\text{--}\text{CO}\text{--}\text{C}(\text{OH})\text{--}\text{NH}\text{--}\text{CO}_2\text{H}$  (Na salt; 12% and 16%, respectively). (II) contains a red dye, decomp.  $>300^\circ$ , which is difficult to remove but is obtained pure after catalytic dehydrogenation (yield up to 8%). Hot  $\text{Ba}(\text{OH})_2$  only very slowly decomposes (II).

VII. 2 : 4 : 5-Triamino-6-hydroxypyrimidine and  $\text{H}_2\text{C}_2\text{O}_4$  at  $140\text{--}260^\circ$  give (I) (90%) and thence deiminoleucopterin (V). "Guanopter" is really isoguanine; in boiling HCl it gives xanthine. X-Ray spectra of (V) and (I) from different sources support the identity. Structures are discussed in both papers. R. S. C.

**Oxidation of pyrrole derivatives with lead tetra-acetate. New porphyrin syntheses.** W. Siedel and F. Winkler (*Annalen*, 1943, 554, 162—201).—Gradual addition of  $\text{Pb}(\text{OAc})_4$  to Et 2 : 4-dimethyl-3-ethylpyrrole-5-carboxylate in  $\text{AcOH}$  at  $>20\text{--}25^\circ$  gives Et 2-hydroxymethyl-3-ethylpyrrole-5-carboxylate (I), m.p.  $126\text{--}128^\circ$ , converted by  $\text{Ac}_2\text{O}$  at  $100^\circ$  into the acetate, m.p.  $135\text{--}136^\circ$ , and by 2N-HCl in boiling EtOH into Et<sub>2</sub> 4 : 4'-dimethyl-3 : 3'-diethylpyrromethane-5 : 5'-dicarboxylate, m.p.  $128^\circ$ . (I) and Me opsopyrrole-carboxylate condense in  $\text{Ac}_2\text{O}$  at  $100^\circ$  to Me 1' : 6'-dicarbethoxy-1 : 3 : 6-trimethyl-2 : 5-diethyltripyrrol-4-propionate, m.p.  $152\text{--}163^\circ$ , becomes yellow at  $52^\circ$ . Alkaline hydrolysis of (I) leads to the relatively stable acid (II), m.p.  $155^\circ$ , which could not be recrystallised. It is decarboxylated when heated at  $160\text{--}170^\circ$ , when boiled with MeOH containing HBr through which air is passed, when kept for several days in MeOH exposed to air, or when suddenly (but not slowly) heated at  $180^\circ$  in a high vac. with formation of a mixture of aetioporphylin I (III) and II (IV). When heated with Cu-bronze or ZnO at  $160\text{--}170^\circ$  (II) gives the Cu and Zn complex salts of (III) and (IV). Cryptopyrrole (V) (picrate, m.p.  $135^\circ$ ) is identified among the products of the dry decarboxylation of (II). The intermediate aetioporphylinogen, blackens at  $200^\circ$  after becoming discoloured at  $140^\circ$ , can be isolated if condensation by HBr in MeOH is effected rapidly; this passes slowly into (III) and (IV) when exposed to air but is relatively stable when dry. Condensation of (V) with 3-methyl-4-ethylpyrrole-5-aldehyde by 48% HBr gives 3' : 4' : 5'-trimethyl-3 : 4'-diethylpyrromethene hydrobromide, m.p.  $178\text{--}179^\circ$ , and with 2-bromo-3-methyl-4-ethylpyrrole-5-aldehyde affords 5-bromo-3' : 4' : 5'-trimethyl-3 : 4'-diethylpyrromethene hydrobromide (VI), m.p.  $216\text{--}217^\circ$  (decomp.). Bromination of either pyrromethene in  $\text{AcOH}$  affords a mixture of  $\sim 90\%$  of the perbromide (VII), m.p.  $147\text{--}148^\circ$ , of (VI) and  $\sim 10\%$  of 5-bromo-3' : 4'-dimethyl-5'-bromo-methyl-3 : 4'-diethylpyrromethene hydrobromide, m.p.  $>300^\circ$  [also obtained when (VII) is boiled with  $\text{AcOH}$ ]. The mixture is converted by boiling  $\text{HCO}_2\text{H}$  into homogeneous (III). Analogous condensations using 2 : 3-dimethyl-4-ethylpyrrole give respectively 4 : 4' : 5'-trimethyl-3 : 3'-diethylpyrromethene hydrobromide, m.p.  $181^\circ$ , softening, and its 5-Br-derivative, swells at  $247^\circ$ , softens at  $216^\circ$ ; either pyrromethene gives the perbromide, m.p.  $>300^\circ$ , converted by boiling  $\text{AcOH}$  into 5-bromo-4 : 4'-dimethyl-5'-bromomethyl-3 : 3'-diethylpyrromethene hydrobromide, softens indistinctly at  $285^\circ$ , darkens at  $180^\circ$ , and by  $\text{HCO}_2\text{H}$  into homogeneous (IV). (III) appears to be dimorphous. Oxidation of Et 2 : 3-dimethyl-4-ethyl-

pyrrole-5-carboxylate by  $\text{Pb}(\text{OAc})_4$  in  $\text{AcOH}$  and treatment of the product with  $\text{Ac}_2\text{O}$  gives Et 3-methyl-2-acetoxymethyl-4-ethylpyrrole-5-carboxylate, m.p.  $106^\circ$ , hydrolysed ( $\text{KOH}\text{--}\text{MeOH}$ ) to 3-methyl-2-hydroxymethyl-4-ethylpyrrole-5-carboxylic acid, m.p.  $135^\circ$  (decomp.), which gives a mixture of (III) and (IV) when heated rapidly to  $160\text{--}170^\circ$  or treated with 48% HBr in boiling MeOH. A similar mixture also results from 4 : 4'-dimethyl-3 : 3'-diethylpyrromethane-5 : 5'-dicarboxylic acid and  $\text{MeOH}\text{--}\text{HBr}$ . 5-Carbethoxy-2 : 4-dimethylpyrrole-3-propionic acid is oxidised [ $\text{Pb}(\text{OAc})_4$  in  $\text{AcOH}$ ] to the 2-hydroxymethyl compound, m.p.  $277\text{--}278^\circ$ . 5-Carboxy-4-methyl-2-hydroxymethylpyrrole-3-propionic acid does not melt when slowly heated but immediately melts with decomp. when placed on a plate heated at  $200^\circ$ ; when heated at  $240\text{--}250^\circ$  or treated with 48% HBr-MeOH it gives coproporphyrin I Me<sub>4</sub> ester (VIII) (with some coproporphyrin) in somewhat impure form and in small yield. 2-Aldehyde-3-methylpyrrole-4-propionic acid and 2 : 4-dimethylpyrrole-3-propionic acid are condensed by 48% HBr to 3 : 3' : 5'-trimethylpyrromethene-4 : 4'-dipropionic acid hydrobromide, m.p.  $200^\circ$  (decomp.), darkens at  $150\text{--}160^\circ$ , which is converted by Br in  $\text{AcOH}$  into the 5-Br-compound, softens at  $219\text{--}220^\circ$  after darkening, and thence by treatment with  $\text{AcCO}_2\text{H}$  at  $180^\circ$  into coproporphyrin II Me<sub>4</sub> ester, m.p.  $292^\circ$ , softens at  $280^\circ$ , which differs appreciably from (VIII) in Debye-Scherrer diagram. Et 2 : 3 : 4-trimethylpyrrole-5-carboxylate is oxidised [ $\text{Pb}(\text{OAc})_4$ ] and then acetylated to Et 3 : 4-dimethyl-2-acetoxymethylpyrrole-5-carboxylate, m.p.  $132^\circ$ ; the corresponding acid, m.p.  $\sim 135^\circ$  (decomp.), passes at  $160\text{--}170^\circ$  into octamethylporphyrin. Gradual addition of 2-methyl-3 : 4-dipropylpyrrole followed by  $\text{ClCO}_2\text{Et}$  to  $\text{MgEtBr}$  in  $\text{Et}_2\text{O}$  gives Et 2-methyl-3 : 4-dipropylpyrrole-5-carboxylate, m.p.  $99\text{--}101^\circ$ , oxidised by  $\text{Pb}(\text{OAc})_4$  in  $\text{AcOH}$  at room temp. to Et 2-acetoxymethyl-3 : 4-dipropylpyrrole-5-carboxylate, m.p.  $97^\circ$ . This appears to be hydrolysed and decarboxylated simultaneously by  $\text{KOH}\text{--}\text{MeOH}$  and the alkali-insol. product is transformed by 48% HBr in MeOH into octapropylporphyrin, m.p.  $290^\circ$ , softens at  $280^\circ$ . Et 2 : 4-dimethylpyrrole-5-carboxylate is oxidised to Et 4-methyl-2-acetoxymethylpyrrole-5-carboxylate, m.p.  $110\text{--}112^\circ$  (sublimation); the free acid does not give a porphyrin according to the previous methods or when heated with  $\text{AcOH}$  in a sealed tube. Et 2-acetoxymethylpyrrole-5-carboxylate, m.p.  $98\text{--}99^\circ$ , obtained by oxidation of the 2-Me compound, is hydrolysed by 5%  $\text{Na}_2\text{CO}_3$  in presence of  $\text{COMe}_2$  to Et 2-hydroxymethylpyrrole-5-carboxylate, m.p.  $83\text{--}84^\circ$ , and by  $\text{NaOH}$  in aq. MeOH to 2-hydroxymethylpyrrole-5-carboxylic acid, m.p.  $>300^\circ$ , which could not be condensed to a porphyrin. By use of a larger proportion of  $\text{Pb}(\text{OAc})_4$  it is possible to convert  $\alpha\text{-Me}$  into  $\alpha\text{-CHO}$ ; the prep. of Et 2-aldehyde-4-methyl-3-ethylpyrrole-5-carboxylate, m.p.  $90^\circ$ , and 5-carbethoxy-2-aldehyde-4-methylpyrrole-3-propionic acid, m.p.  $173^\circ$ , is recorded. The yield of Et 2-aldehydopyrrole-5-carboxylate, m.p.  $74\text{--}75^\circ$ , is less satisfactory.  $\text{Pb}(\text{OAc})_4$  does not appear suitable for the conversion of  $\alpha\text{-Me}$  into  $\alpha\text{-CO}_2\text{H}$ . H. W.

**Chlorophyll. XCIII. Conversion of porphyrins into dihydroxy-chlorins by the action of osmium tetroxide.** H. Fischer and H. Eckoldt (*Annalen*, 1940, 544, 138—162).— $\text{OsO}_4$  adds to porphyrins in  $\text{Et}_2\text{O}\text{--}\text{C}_6\text{H}_5\text{N}$  to give compounds, hydrolysis of which by  $\text{Na}_2\text{SO}_3$  in boiling aq. MeOH and then esterification ( $\text{CH}_2\text{N}_2$ ) gives dihydroxy-chlorins (A) (5—20%), the structure of which is proved by reactions given below and by absorption spectra (figures in parentheses are absorption max. in order of intensity). (A) differ from the parent porphyrins by 2 additional OH in ring IV. (A) are prepared from the compounds named as follows: aetioporphylin (hydrolysis by aq.  $\text{Na}_2\text{SO}_3$ ; no esterification), m.p.  $>300^\circ$  (6463, 4928, 5935, 5230, 6151, and 5443 A. in  $\text{C}_6\text{H}_5\text{N}\text{--}\text{Et}_2\text{O}$ ); from deuteroporphylin Me<sub>4</sub> ester, m.p.  $229^\circ$  (6413, 4914, 5868, 5198, 6112, and 5415 A. in  $\text{C}_6\text{H}_5\text{N}\text{--}\text{Et}_2\text{O}$ ; Cu salt, m.p.  $208\text{--}212^\circ$ ) (a compound having absorption max. at 6720, 4892, 5215, 6107, and 6377 A. in  $\text{Et}_2\text{O}\text{--}\text{C}_6\text{H}_5\text{N}$  is also formed); from coproporphyrin, (I), m.p.  $251^\circ$  [6438, 4953, 5901, 5248, 6138, and 5449 A. in  $\text{Et}_2\text{O}\text{--}\text{C}_6\text{H}_5\text{N}$ ; Bz derivative (6507, 4991, 5310, 5931, 6236, and 5675 A. in  $\text{Et}_2\text{O}$ ); from phylloporphyrin, compounds, m.p.  $286^\circ$  (6433, 5042, 5895, and 5383 A. in  $\text{Et}_2\text{O}\text{--}\text{C}_6\text{H}_5\text{N}$ ; Cu salt, m.p.  $233^\circ$ ), and m.p.  $201\text{--}205^\circ$  (6491, 5466, 5940, 5248, 4968, and 6175 A. in  $\text{Et}_2\text{O}\text{--}\text{C}_6\text{H}_5\text{N}$ ); from rhodoporphylin Me<sub>2</sub> ester, (II), m.p.  $262^\circ$  (5121, 5457, 6354, 5830, and 6051 A. in  $\text{Et}_2\text{O}\text{--}\text{C}_6\text{H}_5\text{N}$ ; Cu salt, m.p.  $233^\circ$ ; Bz derivative (6453, 5502, 5120, and 5871 A. in  $\text{Et}_2\text{O}$ ). All these products are reduced by a little HI in  $\text{AcOH}$  at  $100^\circ$  to the original porphyrins. (I) and (II) do not react with  $\text{NH}_2\text{OH}$ . In  $\text{HBr}\text{--}\text{AcOH}$ , (I) gives a red compound (5021, 5348, 5673, and 6222 A. in  $\text{Et}_2\text{O}$ ), and (II) gives a red compound (5489, 5095, 5751, and 6355 A. in  $\text{Et}_2\text{O}$ ). Oleum converts (II) into an anhydro-compound,  $\text{C}_{34}\text{H}_{38}\text{O}_5\text{N}_4$  (5573, 6375, 5210, 5800, and 6106 A. in  $\text{Et}_2\text{O}$ ; also obtained by conc. HCl), and (I) into a substance (6411, 5412, 5065, 5828, and 6116 A. in  $\text{Et}_2\text{O}$ ). The absorption spectra of the  $(\text{OH})_2$ -compounds from pyrroporphyrin and mesoporphyrin are almost identical; the  $\epsilon$  at  $\sim 640$  m $\mu$ . is  $3.5\text{--}4.0 \times 10^{-4}$ , but nowhere else  $>1.0 \times 10^{-4}$ ; the similarity to mesopyrrochlorin is very great. "Propylrhodin" gives (as above) a compound,  $\text{C}_{34}\text{H}_{44}\text{O}_5\text{N}_4$ , m.p.  $223^\circ$  after sintering (6710, 5073, 5405, and 6084 A. in  $\text{Et}_2\text{O}\text{--}\text{C}_6\text{H}_5\text{N}$ ); mesorhodin gives a compound,  $\text{C}_{35}\text{H}_{40}\text{O}_5\text{N}_4$ , m.p.  $184^\circ$ . Protoporphyrin Me<sub>2</sub> ester, m.p.  $223^\circ$ , is obtained ( $\sim 50\%$ ) directly from haemin by successive...

MeOH, HCl-MeOH, and  $\text{CH}_3\text{N}_2\text{-Et}_2\text{O}$ ; with  $\text{MgBr-OPr}$  it gives the phyllin, m.p. 245° (cf. A., 1939, III, 343); deuteroporphyrin  $\text{Me}_2$  ester gives similarly the phyllin, m.p. 248°. With  $\text{Mn(OAc)}_2$  in warm AcOH actio- and meso-porphyrin  $\text{Me}_2$  ester give Mn salts, m.p. >330° and 266°, respectively. R. S. C.

**Nucleic acids. XVIII. Existence of guanineuridylic acid.** H. Bredereck, E. Berger, and F. Richter (*Ber.*, 1941, 74, [B], 338—342).—The existence of guanineuridylic acid is maintained (cf. Levene *et al.*, A., 1940, II, 27; Gulland, *ibid.*, 235). The yield of product (I) obtained by deaminating yeast nucleic acid (II) is improved (cf. A., 1939, III, 326) from 30 to 47.3%; the remainder is lost in the isolation of (I). The same method of isolation applied to (II) gave a yield of 49.5%. (I) contains N and P in the ratio 1.35 (calc. 1.35) and has an equiv. of ~4.3. Thymonucleic acid (III) gives similar yields of deaminated product [N:P = 1.26 (calc. 1.35); equiv. ~4.4]. (II) and (III) are thus completely deaminated but the tetranucleotide structure is preserved; hence (II) and (III) do not contain N-P linkings. Cleavage of some specimens of (II) with aq.  $\text{C}_2\text{H}_5\text{N}$  at 100° gives (no details) guanylic acid (G) and a trinucleotide (IV). Further cleavage of (IV) does not afford a dinucleotide but adenylic acid (A) appears to be liberated first. Thus, (II) and (IV) contain (G) and (A), respectively, as end-groups. (II) probably contains the combination (G)-uridylic acid-cytidylic acid-(A). H. B.

**Nucleic acids. XIX. Enzymic and chemical preparation of nucleosides from yeast nucleic acid.** H. Bredereck, A. Martini, and F. Richter (*Ber.*, 1941, 74, [B], 694—697).—Details are given for the isolation of guanosine, adenosine, cytidine, and uridine from the hydrolysate obtained from yeast nucleic acid (I) and an enzyme prep. (from sweet almonds). The same nucleosides are also obtained in approx. the same or a little higher yield from (I) and boiling aq.  $\text{C}_2\text{H}_5\text{N}$  (1:1 vol.) for 4½ days. Hydrolysis of (I) with even very dil. NaOH is unsatisfactory since much deamination occurs. H. B.

**Morpholine periodide.**—See B., 1941, III, 256.

**Phenothiazines.**—See B., 1943, II, 310.

**Carbocyanines.**—See B., 1943, II, 312.

**Ultra-violet absorption of dyes in solution.**—See A., 1943, I, 271.

**Light absorption and energy propagation by loose complexes in organic dyes.**—See A., 1943, I, 297.

**Quinoxaline cyanines. II.** A. H. Cook and C. A. Perry. III. A. H. Cook and R. F. Naylor (*J.C.S.*, 1943, 394—397, 397—401; cf. A., 1943, II, 47).—II. 3-Keto-2-methyl-3:4-dihydroquinoxaline and its 4-N-Me and -Ph compounds give quaternary salts by addition to the basic N in the 1-position. In these salts the 2-Me is reactive and has been condensed with  $\text{HCO}_2\text{H}$  derivatives and aldehydes or equiv. compounds to give symmetrical and unsymmetrical oxygenated cyanines. Except for diminished solubility these deep blue dyes resemble those derived from true quinoxalines. The following are described: [2-(3-hydroxy-1-methylquinoxaline)][4-dimethylaminophenyl]dimethincyanine iodide, m.p. 225—227°; [2-(3-keto-1-methyl-3:4-dihydroquinoxaline)][2-(1:3:3-trimethylindoline)]trimethincyanine iodide; [bis-2-(3-hydroxy-1-methylquinoxaline)]trimethincyanine acetate, m.p. 280° (decomp.); [2-(3-keto-1-methyl-3:4-dihydroquinoxaline)][2-(1-methylquinoline)]-, m.p. 246°, [2-(3-hydroxy-1-methylquinoxaline)][2-(1-methylbenzoxazole)]-, m.p. 244°, and [2-(3-hydroxy-1-ethylquinoxaline)][2-(1-ethylbenzthiazole)]trimethincyanine iodide, m.p. 260°; 2-keto-1:3-dimethyl-1:2-dihydroquinoxaline methiodide, m.p. 178° (decomp.); [2-(3-keto-1:4-dimethyldihydroquinoxaline)][4-dimethylaminophenyl]dimethincyanine sulphate (base, m.p. 186°), and [2-(1:3:3-trimethylindoline)]trimethincyanine chloride, m.p. 135°; [2-bis-(3-keto-1:4-dimethyldihydroquinoxaline)]trimethincyanine sulphate, m.p. 227°; [2-(3-keto-1-methyl-1-ethyldihydroquinoxaline)][2-(1-ethylbenzthiazole)]trimethincyanine iodide, m.p. 180°; [2-(3-keto-4-phenyl-1-methyldihydroquinoxaline)][4-dimethylaminophenyl]dimethincyanine chloride, m.p. 193—199° (base, m.p. 210°; corresponding Et chloride, m.p. 281°); [2-(3-keto-4-phenyl-1-methyl-3:4-dihydroquinoxaline)][2-(1:3:3-trimethylindoline)]trimethincyanine chloride, m.p. 252°, [2-(1-methylquinoline)]trimethincyanine sulphate, m.p. 244° (decomp.), and [2-(1-methylbenzthiazole)]trimethincyanine chloride, m.p. 235° (decomp.); [bis-2-(3-keto-4-phenyl-1-methyldihydroquinoxaline)]trimethincyanine sulphate, m.p. 287°; and 2-keto-3-benzyl-1:2-dihydroquinoxaline, m.p. 196°, and the 2-keto-1-phenyl compound, m.p. 166°.

III. Two quinoxalinemonomethincyanines have been obtained but attempts to extend the series have been unsuccessful. Several quinoxalines carrying reactive Me have been condensed with  $\text{Et}_2\text{C}_2\text{O}_4$  and the resulting pyruvic acids or esters converted into diquinoxalinylmethanes by reaction with aromatic *o*-diamines. Although it has not been possible to quaternise these compounds to obtain monomethincyanines, the striking colours of their acid solutions are probably indicative of the colour of the unprepared cyanines. The following are described: [2-(1-methylbenzthiazole)][2-(3-keto-1:4-dimethyl-3:4-dihydroquinoxaline)]monomethincyanine iodide, m.p. 242°, and [2-(1-phenyl-3-methylquinoxaline)]monomethincyanine iodide, m.p. 188°; 1-phenyl-3-methylquinoxaline-2-aldoxime

chloride, m.p. 283°; Et 2-keto-1-methyl-1:2-dihydroquinoxaline-3-pyruvate, m.p. 170° (acid, m.p. 218°; oxime, m.p. 158.5°; phenylhydrazone, m.p. 202°), and its condensation product, m.p. 228°, with *o*- $\text{OH-C}_6\text{H}_4\text{-CHO}$ , 3-(2-keto-1-methyldihydroquinoxalinyll)-3-(2-keto-dihydroquinoxalinyll)methane, m.p. 355° and -1-phenyldihydroquinoxalinyll)methane, m.p. 300°; bis-3-(2-keto-1-methyl-1:2-dihydroquinoxalinyll)methane, m.p. 331°; Et 2-keto-1-phenyl-1:2-dihydroquinoxaline-3-pyruvate, m.p. 224° [acid, m.p. 226° (decomp.)]; 3-(2-keto-1-phenyldihydroquinoxalinyll)-3-(2-ketodihydroquinoxalinyll)methane, m.p. 372°; Et 3-methyl-4-quinazolonyl-2-pyruvate, m.p. 173° (phenylhydrazone, m.p. 168—169°); 2-(3-methyl-4-quinazolonyl)-3-(2-ketodihydroquinoxalinyll)methane, m.p. 354°, -1-methyl-, m.p. 293°, and -1-phenyl-dihydroquinoxalinyll)methane, m.p. 265°; 2-carbethoxy-3-(3'-methyl-2'-quinoxalyl)indole, m.p. 153°, and -(2'-keto-1'-methyl-dihydro-3'-quinoxalyl)indole, m.p. 246°; and 3-(2-keto-1-methyldihydroquinoxalinyll)-3-(2-keto-1-phenyl-, m.p. 290° (decomp.), and -(2-keto-dihydroquinoxalinyll)methane hydrochloride, decomp. >300°. F. R. S.

## VII.—ALKALOIDS.

**Constitution of  $\psi$ -conhydrine.** E. Späth and R. Lorenz (*Ber.*, 1941, 74, [B], 599—603).—The structure of  $\psi$ -conhydrine [3-hydroxy-6-*n*-propylpiperidine] is now proved (cf. A., 1933, 516). Dihydro- $\psi$ -conhydrinemethine (*loc. cit.*) is  $\alpha$ -dimethylamino-octan- $\beta$ -ol since it is oxidised (aq.  $\text{AcOH-CrO}_3$  at 70°) to  $\alpha$ -dimethylamino-octan- $\beta$ -one (I), b.p. 75—80°/10 mm. (aurichloride, m.p. 83.5—84.5°; methiodide, m.p. 156—156.5°; methopicate, m.p. 114—116°). *n*- $\text{C}_6\text{H}_{13}\text{-COCl}$  and  $\text{Et}_2\text{O-CH}_2\text{N}_2$  give  $\alpha$ -chloro-octan- $\beta$ -one, b.p. 91—96°/10 mm. (and surprisingly some *n*- $\text{C}_6\text{H}_{13}\text{-CO}_2\text{Et}$ ), converted by aq.  $\text{NHMe}_2$  into (I). H. B.

**The alkaloid in *Eclipta alba* (Hassk).** S. N. Pal and M. Narasimham (*J. Indian Chem. Soc.*, 1943, 20, 181).—3.1 g. of alkaloid, extracted from 4 kg. of the air-dried plant, was nicotine. S. A. M.

**Synthesis in the series of cinchona alkaloids. II. Synthesis of 6'-methoxyruban-9-ol.** V. Prelog, R. Seiwert, S. Heimbach-Juhász, and P. Stern (*Ber.*, 1941, 74, [B], 647—652).—The yield of product from Et quinate and  $\beta$ -1-benzoyl-4-piperidylpropionate depends greatly on the quality of the NaOEt used for condensation. Na powder in boiling  $\text{C}_6\text{H}_6$  gives 88% of the CO-ester, hydrolysed to 6'-methoxyrubatoxan-9-one (I). With Br in 48% HBr and light (quartz lamp) (I) gives the 8-Br-derivative, converted by 5%  $\text{Na}_2\text{CO}_3$  +  $\text{Et}_2\text{O}$  then *n*-NaOH into 6'-methoxyruban-9-one (II), m.p. 90—91° [picrate, m.p. 211—211.5° (lit. 173—174°); picrolonate, m.p. 226° (lit. 148—150°)] (cf. Rabe *et al.*, A., 1922, i, 361). Bromination in the dark followed by the above procedure gives (II) and (probably) 5'-bromo-6'-methoxyrubatoxan-9-one, m.p. 270—271°. Reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ , MeOH) of (II) affords mainly 6'-methoxyruban-9-ol-A (III) (picrate, m.p. 224—225°) and a little -B [picrate, m.p. 226°, and 210° with that of (III)]. The dihydrochloride, m.p. 239—240°, of (III) is active against bird malaria and possesses pharmacological similarity to quinine (e.g., blood pressure; action on smooth muscle) and quinidine (e.g., action on frog's heart). The difference between these findings and those of Rabe *et al.* (see below) is unexplained. H. B.

**Cinchona alkaloids. XXXII. Synthesis of 6'-methoxyruban-9-ols; mode of action of quinine and quinidine.** P. Rabe and G. Hagen (*Ber.*, 1941, 74, [B], 636—647).—Et  $\beta$ -1-benzoyl-4-piperidylpropionate (improved prep.) is condensed (NaOEt; no solvent) with Et quinate and the product hydrolysed (18% HCl) to 6'-methoxyrubatoxan-9-one, which with Br in 40% HBr gives the impure 8-Br-derivative dihydrobromide. This with aq.  $\text{Na}_2\text{CO}_3$  +  $\text{Et}_2\text{O}$  at 0° affords 6'-methoxyruban-9-one (I), m.p. 89° (cf. A., 1922, i, 361), and some ? dibromomethoxyrubanone, m.p. 66°. Cryst. (I) is a racemate; in solution (or when molten) it gives by a keto-enol change two enantiostereoisomerides and two *cis-trans*-isomerides. Reduction ( $\text{H}_2$ , Pd-black, 3—4% HCl) of (I) affords a mixture of four stereoisomeric 6'-methoxyruban-9-ols. The (+ +)-(— —)-racemate, ( $\text{C}_{18}\text{H}_{23}\text{O}_2\text{N}_2$ ) $\cdot 6\text{H}_2\text{O}$  (II), m.p. (anhyd.) 179° (the signs refer to the configuration of  $\text{C}_{(8)}$  and  $\text{C}_{(9)}$  respectively), is readily separated from the oily (+ —)-(— +)-racemate (III) through its sparing solubility in moist  $\text{Et}_2\text{O}$ . (II) is resolved through the H *d*- and *l*-tartrates whilst (III) is resolved through the neutral dianisoyl-*d*- and *l*-tartrates. The dianisoyl-*d*- and *l*-tartaric acids used have  $[\alpha]_D^{20}$  -166° and  $[\alpha]_D^{20}$  +148° in EtOH, respectively. Thus are obtained (+ +)-6'-methoxyruban-9-ol (IV) (+ $\text{H}_2\text{O}$ ), m.p. (anhyd.) 187°,  $[\alpha]_D^{20}$  +173.8° in EtOH [hydrochloride, m.p. 221° (decomp.),  $[\alpha]_D^{20}$  +130.3° in EtOH; H *d*-tartrate (+3 $\text{H}_2\text{O}$ ), m.p. 150—155° (decomp.) (sinters 115°),  $[\alpha]_D^{20}$  +124.1° in EtOH, m.p. (anhyd.) ~169° (decomp.)], (— —)-6'-methoxyruban-9-ol (V), m.p. 187°,  $[\alpha]_D^{20}$  -173.5° in EtOH [hydrochloride, m.p. 219° (decomp.),  $[\alpha]_D^{20}$  -130.4° in EtOH; H *l*-tartrate (+3 $\text{H}_2\text{O}$ ), m.p. 150—155° (decomp.) (sinters 107°),  $[\alpha]_D^{20}$  -123.7° in EtOH; *l*-tartrate (+ $\text{H}_2\text{O}$ ), m.p. 234° (decomp.),  $[\alpha]_D^{20}$  -135.1° in  $\text{H}_2\text{O}$ ; H dianisoyl-*d*-tartrate (+MeOH), m.p. 188° (decomp.),  $[\alpha]_D^{20}$  (MeOH-free) -158.8° in EtOH], (+ —)-6'-methoxyruban-9-ol, oil,  $[\alpha]_D^{18}$  +23.5° in EtOH [hydrochloride, m.p. 221—223°

(decomp.),  $[\alpha]_D^{20} + 12.57^\circ$  in EtOH; *dianisoyl-d-tartrate* (+5H<sub>2</sub>O), m.p. 155° (decomp.),  $[\alpha]_D^{20} - 66.4^\circ$  in EtOH, and (—) 6'-methoxy-ruban-9-ol, an oil,  $[\alpha]_D^{20} - 23.25^\circ$  in EtOH [*hydrochloride*, m.p. 222—223°,  $[\alpha]_D^{20} - 14.4^\circ$  in EtOH; H *d-tartrate*, m.p. 135° (decomp.),  $[\alpha]_D^{20} + 11.68^\circ$  in H<sub>2</sub>O; *dianisoyl-l*, m.p. ~155° (decomp.),  $[\alpha]_D^{20} + 50.02^\circ$  in EtOH, and *-d-tartrate*, m.p. 125—143° (decomp.),  $[\alpha]_D^{20} - 73.29^\circ$  in EtOH]. These are converted by HCl-CHCl<sub>3</sub> and then PCl<sub>5</sub> at room temp. into the respective 9-chloro-6'-methoxyrubans, m.p. 99° (sintering),  $[\alpha]_D^{20} + 25.6^\circ$  in EtOH (VI), m.p. 98—100° (sintering),  $[\alpha]_D^{20} - 24.71^\circ$  in EtOH (VII), m.p. ~101—102°,  $[\alpha]_D^{20} + 79.1^\circ$  in EtOH (VIII), and m.p. ~101—102°,  $[\alpha]_D^{20} - 79.02^\circ$  in EtOH (IX). Reduction (H<sub>2</sub>, Pd-CaCO<sub>3</sub>, EtOH-KOH) of (VI) and (VIII) gives (+)-6'-methoxyruban,  $[\alpha]_D^{20} + 129^\circ$  in EtOH (hydrate, m.p. 66°); (VII) and (IX) similarly give (—)-6'-methoxyruban,  $[\alpha]_D^{20} - 129.5^\circ$  in EtOH (no hydrate). (V) has no action against bird malaria. (IV) has a surprisingly favourable action in disturbances of cardiac rhythm.

H. B.

**Cinchona alkaloids. XXXIII. heteroQuinine, a 1 : 1-hydramine.** P. Rabe (*Ber.*, 1941, 74, [B], 725—728).—Fractional distribution of quinine ("purissimum praeccipitatum") between aq. HCO<sub>2</sub>H and Et<sub>2</sub>O gives a little resinous material (most weakly basic part) which yields through its neutral sulphate, m.p. 218° (darkens 210°), 0.006% of heteroquinine (I) (A, R = CH:CH<sub>2</sub>, R' = 6-methoxy-4-quinolyl), m.p. 167°. (I) is insol. in alkali hydroxide (distinction from cupreine) and gives the thalleioquine reaction. Attempts to isolate (I) from a viscous product (termed quinoidine) obtained from the mother-liquors after processing cinchona bark were unsuccessful; (I) may have been present since the most weakly basic part, an oil, gave the thalleioquine reaction. Attention is directed to heterohydrocinchonine (A., 1935, 99).

H. B.

**Ergot alkaloids. VII. Alkaloids of the ergotoxine group; ergocryptine, ergocryptine, and ergocornine.** A. Stoll and A. Hofmann (*Helv. Chim. Acta*, 1943, 26, 1570—1601).—Ergotoxine (I) preps. are usually mixtures of three well-defined alkaloids, ergocristine (II), ergocryptine (III), and ergocornine (IV). The name (I) is retained as a group designation for preps. described and used under this name. (I) is treated with two equivs. of *l*-di-*p*-toluoyl-tartaric acid in 90% EtOH, whereby a copious crystallisation of the mixed salts occurs. This is dissolved in abs. EtOH, from which the bulk of the *l*-di-*p*-toluoyltartrate of (II) separates. The main pptn. of alkaloidal salts occurs when the mother liquor is diluted to 80% with H<sub>2</sub>O. A small further quantity is secured by diluting the filtrate to 50%, leaving in solution only a small proportion of salt which is recovered as base and united with subsequent end fractions. The operations are repeated with the heterogeneous cryst. fractions and the most freely sol. portions are treated with abs. and then with 70% MeOH. The method is nearly quant. A detailed description of the treatment of various preps. of (I) is given. The *l*-di-*p*-toluoyltartrates are more stable than other alkaloidal salts but their stability is only relative. To prevent transformation into the dextrorotatory isomerides of the alkaloids or their oxidative decomp. by air or light and to obtain lightly coloured materials the salts must remain in solution for the least possible time; if crystallisation does not occur within a few min. it generally does not occur at all. Unless absolutely necessary, the solutions should not be warmed and, if necessary, the heating should be restricted to a few sec. Solid substances and, particularly, solutions should be protected from light. The following are described: (II), best cryst. from COMe<sub>2</sub> from which it separates with 1 COMe<sub>2</sub>, m.p. 160—175° (decomp.),  $[\alpha]_D^{20} - 183^\circ$ ,  $[\alpha]_{5461}^{20} - 217^\circ$  in CHCl<sub>3</sub>,  $[\alpha]_D^{20} - 93^\circ$ ,  $[\alpha]_{5461}^{20} - 107^\circ$  in C<sub>5</sub>H<sub>5</sub>N [*l*-di-*p*-toluoyltartrate, m.p. 191° (decomp.),  $[\alpha]_D^{20} + 58^\circ$  in abs. EtOH; hydrochloride, m.p. 205° (decomp.); phosphate, m.p. 195° (decomp.); ethanesulphonate, m.p. 207° (decomp.); *d-tartrate*, m.p. (indef.) 185—190° (decomp.)]; ergocristine, new m.p. 226° (decomp.),  $[\alpha]_D^{20} + 462^\circ$ ,  $[\alpha]_{5461}^{20} + 576^\circ$  in C<sub>5</sub>H<sub>5</sub>N,  $[\alpha]_D^{20} + 383^\circ$ ,  $[\alpha]_{5461}^{20} + 479^\circ$  in COMe<sub>2</sub>; (III), m.p. 212° (decomp.),  $[\alpha]_D^{20} - 187^\circ$ ,  $[\alpha]_{5461}^{20} - 226^\circ$  in CHCl<sub>3</sub>,  $[\alpha]_D^{20} - 112^\circ$ ,  $[\alpha]_{5461}^{20} - 133^\circ$  in C<sub>5</sub>H<sub>5</sub>N [*l*-di-*p*-toluoyltartrate, m.p. 186° (decomp.),  $[\alpha]_D^{20} + 103^\circ$  in abs. EtOH; hydrochloride, m.p. (indef.) 208° (decomp.); phosphate, m.p. 198—200° (decomp.); *d-tartrate*, m.p. (indef.), 209° (decomp.); ethanesulphonate, m.p. 204° (decomp.)], converted by boiling MeOH into ergocryptine, m.p. 240—242° (decomp.)  $[\alpha]_D^{20} + 408^\circ$ ,  $[\alpha]_{5461}^{20} + 508^\circ$  in CHCl<sub>3</sub>,  $[\alpha]_D^{20} + 479^\circ$ ,  $[\alpha]_{5461}^{20} + 596^\circ$  in C<sub>5</sub>H<sub>5</sub>N,  $[\alpha]_D^{20} + 396^\circ$ ,  $[\alpha]_{5461}^{20} + 493^\circ$  in COMe<sub>2</sub>; (IV), m.p. 182—184° (decomp.),  $[\alpha]_D^{20} - 188^\circ$ ,  $[\alpha]_{5461}^{20} - 226^\circ$  in CHCl<sub>3</sub>,  $[\alpha]_D^{20} - 105^\circ$ ,  $[\alpha]_{5461}^{20} - 122^\circ$  in C<sub>5</sub>H<sub>5</sub>N [*l*-di-*p*-toluoyltartrate, m.p. 180—181° (decomp.),  $[\alpha]_D^{20} + 103^\circ$  in abs. EtOH; hydrochloride, m.p. 223° (decomp.); hydrobromide, m.p. 225° (decomp.); phosphate, m.p. 190—195° (decomp.); non-cryst. *d-tartrate*; very stable and cryst. ethanesulphonate, m.p. 209° (decomp.)], converted by boiling MeOH into ergocornine, m.p. 228° (decomp.),  $[\alpha]_D^{20} + 409^\circ$ ,  $[\alpha]_{5461}^{20} + 512^\circ$  in CHCl<sub>3</sub>,  $[\alpha]_D^{20} + 500^\circ$ ,  $[\alpha]_{5461}^{20} + 624^\circ$  in C<sub>5</sub>H<sub>5</sub>N,  $[\alpha]_D^{20} + 414^\circ$ ,  $[\alpha]_{5461}^{20} + 517^\circ$  in COMe<sub>2</sub>. Photomicrographs of the crystals of the six alkaloids are given. A historical survey of (I) and ergotinine is given and the literature data are examined critically from the viewpoint of the new observations. M.p. are corr.

H. W.

**Ergot alkaloids. VIII. Products of the fission of ergocristine, ergocryptine, and ergocornine.** A. Stoll, A. Hofmann, and B. Becker (*Helv. Chim. Acta*, 1943, 26, 1602—1613).—Alkaline hydrolysis of ergocristine (I) gives *d*-lysergic acid (II), NH<sub>3</sub>, COPrβ·CO<sub>2</sub>H, *dl*-proline, and *dl*-phenylalanine. The mol. sum of these 5 products less 4 mols. of H<sub>2</sub>O is C<sub>35</sub>H<sub>39</sub>O<sub>5</sub>N<sub>4</sub>, identical with the formula determined analytically. (I) thus contains the structural units present in ergotinine preps. Treatment of ergocryptine (III) with N<sub>2</sub>H<sub>4</sub> leads to *dl*-isolysergic acid in good yield. Thermal fission gives COPrβ·CO·NH<sub>2</sub> and a non-distillable, viscous oil which affords *l*-leucyl-*d*-prolyl-lactam, m.p. 148—150°,  $[\alpha]_D^{20} + 92^\circ$ ,  $[\alpha]_{5461}^{20} + 109^\circ$  in H<sub>2</sub>O, hydrolysed by acid to *l*-leucine, m.p. 280° (decomp.),  $[\alpha]_D^{20} - 10.8^\circ$ ,  $[\alpha]_{5461}^{20} - 13.4^\circ$  in H<sub>2</sub>O, and *d*-proline (IV), characterised as the salt C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub>·CdCl<sub>2</sub>·H<sub>2</sub>O, m.p. 210°. The results agree with the analytically established formula C<sub>32</sub>H<sub>41</sub>O<sub>5</sub>N<sub>5</sub>. Alkaline hydrolysis of ergocornine (V) affords (II). Its thermal decomp. leads to COPrβ·CO·NH<sub>2</sub> and *l*-valyl-*d*-prolyl-lactam, m.p. 147—149°,  $[\alpha]_D^{20} + 88^\circ$ ,  $[\alpha]_{5461}^{20} + 107^\circ$  in H<sub>2</sub>O, hydrolysed by boiling conc. HCl to *l*(+)-valine,  $[\alpha]_D^{20} + 32^\circ$  in 20% HCl, and (IV), characterised as dimethyl-*d*-prolinebetaine aurichloride, m.p. 245°. Among the ergot alkaloids, the ergotamine group (ergotamine-ergotaminine; ergosine-ergosinine) is characterised by giving AcCO<sub>2</sub>H as α-CO-acid. The ergotoxine group [(I)-ergocristine; (III)-ergocryptine; (V)-ergocornine] gives rise to COPrβ·CO<sub>2</sub>H analogously. Differing in principle but still containing (II) as main component are ergobasine-ergobasine in which (II) is present as the *l*-β-hydroxyisopropylamide.

H. W.

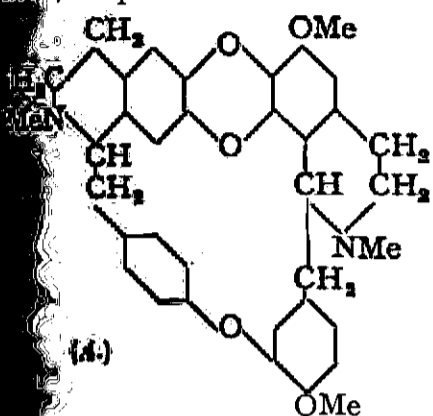
**Veratrine alkaloids. XX. Further correlations in the veratrine group. Relationship between the veratrine bases and solanidine.** L. C. Craig and W. A. Jacobs (*J. Biol. Chem.*, 1943, 149, 451—464; cf. A., 1943, II, 246).—The unsaturated hexacyclic character of the veratrine bases is discussed. Attempts to hydrogenate (H<sub>2</sub>-PtO<sub>2</sub>) germinine (I) failed, but isogerminine (II) gives (PtO<sub>2</sub>-MeOH) dihydroisogerminine, m.p. 277—278° (previous darkening and softening),  $[\alpha]_D^{20} - 61^\circ$  in C<sub>5</sub>H<sub>5</sub>N. Dihydrogerminine, m.p. 265° (shrinks at >258° to a resin),  $[\alpha]_D^{20} - 57^\circ$  in C<sub>5</sub>H<sub>5</sub>N (hydrochloride, decomp. >250°), is obtained from (I) and Na-Bu<sup>o</sup>OH. Rubijervine (III) and isorubijervine (IV) give (H<sub>2</sub>-PtO<sub>2</sub>-MeOH-AcOH) dihydro-rubijervine, m.p. 222° (its Ac<sub>2</sub> derivative, m.p. 216—219°, retains the original basic character), and -isorubijervine, m.p. 244° (previous softening), respectively. (I) and aq. NaOH-MeOH at 50° yield (II), but similar attempts to isomerise (III) or (IV) were unsuccessful. Jervine, C<sub>27</sub>H<sub>39</sub>O<sub>3</sub>N (pentacyclic), remains in a special class, as it reacts as a sec. base and contains <2 conjugated double linkings which can be hydrogenated to tetrahydrojervine. (IV) readily forms a digitonide (cryst. within 30 min.), suggesting a 3(β)-OH group in the A ring of a steroid. (III) yields a digitonide on long keeping, but (I), (II), cevine, and protoverine do not. Veratrine alkaloids behave in some ways differently from solanidine (V) and related compounds. Methylcyclopentenophenanthrene is not isolated from the dehydrogenation of a veratrine base. Dehydrogenation of (V) gives (chromatographic separation) γ-methyl-1 : 2-cyclopentenophenanthrene, m.p. 126—127°, 2-methyl-, m.p. 120—121°, and 1 : 2-dimethyl-phenanthrene, m.p. 146—148°, and a small amount of a substance, C<sub>27</sub>H<sub>41</sub>N or C<sub>28</sub>H<sub>43</sub>N, m.p. 183—197°; no fluorene hydrocarbon was isolated. Constitutions of the veratrine alkaloids are discussed, but they are not clear.

A. T. P.

**Biscoclaurine alkaloids: constitutions of chondodendrine and trilobine.** F. Faltis, L. Holzinger, P. Ita, and R. Schwarz (*Ber.*, 1941, 74, [B], 79—97; cf. A., 1936, 1003).—Chondodendrine is degraded to a mixture of 6 : 4'-dicarboxy-2 : 3-dimethoxy-5-vinyl-diphenyl ether (I) (the sole product from isochondodendrine) and an isomeride (II). To establish the structure of (II) [already degraded to 4-carboxy-2 : 2'-dimethoxydiphenyl ether (III); loc. cit.] as 5 : 5'-dicarboxy-2 : 2'-dimethoxy-4-vinyl-diphenyl ether, it was necessary to synthesise 4 : 5 : 5'-tricarboxy-2 : 2'-dimethoxydiphenyl ether (IV) (cf. King, A., 1939, II, 458). 4 : 5 : 1 : 2-C<sub>6</sub>H<sub>2</sub>Br<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub>, KOMe, and Cu at 170—180° give Me<sub>2</sub> 4-bromo-5-methoxyphthalate (V), m.p. 82—84° [free acid, m.p. 195.5°, effervescing at 192°, purified with difficulty from traces of 4 : 5 : 1 : 2-C<sub>6</sub>H<sub>2</sub>Br<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub>]. isoVanillinoxime, m.p. 145—145.5°, and hot Ac<sub>2</sub>O afford O-acetylvanillonitrile, m.p. 122° (once, at room temp., isovanillinoxime acetate, m.p. 109.5°), hydrolysed (NaOH) to 3 : 4 : 1-C<sub>6</sub>H<sub>3</sub>(OH)(OMe)·CN, m.p. 131.5—132°. Ullmann condensation between (V) and 3 : 4 : 1-C<sub>6</sub>H<sub>3</sub>(OK)(OMe)·CO<sub>2</sub>Me gives little (IV), and 3 : 4 : 1-C<sub>6</sub>H<sub>3</sub>(OMe)<sub>2</sub>·CO<sub>2</sub>H is a troublesome by-product. o-OK·C<sub>6</sub>H<sub>4</sub>·OMe, 3 : 4 : 1-C<sub>6</sub>H<sub>3</sub>Br(OMe)·CO<sub>2</sub>Me (VI), m.p. 95.5—96°, and Cu at 180° give *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Me (VII) mixed with some (VI) and 5-carboxy-2 : 2'-dimethoxydiphenyl ether, m.p. 167.5—168.5° [Me ester, m.p. 59.5—60°; in one experiment the phenolic portion contained (?) 2-bromo-2'-hydroxy-6 : 3'-dimethoxydiphenyl ether, m.p. 160—165°, possibly formed subsequently to transference of Br from (VI) to o-OH·C<sub>6</sub>H<sub>4</sub>·OMe]. (VI), KOPh, and Cu at 190° give some PhOMe, (VII), (VI), and 5-carboxy-2-methoxydiphenyl ether, m.p. 187—187.5° (Me ester, b.p. 120—140°/0.05 mm.). Me 4-bromo-3-methoxybenzoate (VIII), m.p. 55—55.8° (from the acid and CH<sub>2</sub>N<sub>2</sub>), o-ONa·C<sub>6</sub>H<sub>4</sub>·OMe, and Cu at 190° give impure *m*-OMe·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Me, (VIII), and (III), m.p. 163—164°. The Ullmann condensation

between (VI) and *Me*<sub>2</sub> 4-hydroxy-5-methoxyphthalate, m.p. 93—94°, is very unsatisfactory and the main products are (VII) and 4:5:1:2-*C*<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub>. The ordinary diphenyl ether synthesis appears to have reached the limit of its scope in the prep. of these tricarboxylic acids, since transference of halogen and alkyl groups takes place readily as a result of the accumulation of CO<sub>2</sub>Me groups. More satisfactory results are obtained with intermediates of a lower state of oxidation where side-chains can be converted into CO<sub>2</sub>H subsequent to Ullmann condensation. iso*Vanillin semicarbazone*, m.p. 212° (decomp.), NaOEt, and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O at 160° give 1:3:4-*C*<sub>6</sub>H<sub>3</sub>Me(OH)·OMe, which with AcCl and AlCl<sub>3</sub> in PhNO<sub>2</sub> gives 2:4:5:1-*C*<sub>6</sub>H<sub>2</sub>Me(OH)(OMe)·COMe (IX), m.p. 123°. (VI), the K derivative of (IX), and Cu at 190° afford 5'-carbo-methoxy-2:2'-dimethoxy-4-acetyl-5-methyldiphenyl ether, m.p. 131.5—132° (semicarbazone, m.p. 203—203.5° with decomp.); the free acid, m.p. 203—204°, is cautiously oxidised by alkaline KMnO<sub>4</sub>

to the glyoxylic acid, C<sub>18</sub>H<sub>16</sub>O<sub>8</sub>, m.p. 203° (phenylhydrazone, m.p. 187—189°), which is further oxidised (H<sub>2</sub>O<sub>2</sub>) to 4:5'-dicarboxy-2:2'-dimethoxy-5-methyldiphenyl ether (X), m.p. 250—251° (Me<sub>2</sub> ester, m.p. 123—124°). (X) is oxidised by hot alkaline KMnO<sub>4</sub> to (IV), mixed m.p. with the acid from the degradation of chondodendrine showing no depression. The biogenesis of this type of alkaloid is postulated to start with an enzymic dehydrogenation of coclaurine, followed by a continuous series of de-



hydrogenations and methylations via magnoline and trilobamine to tetrandrine and to trilobine, for which (or for isotrilobine) structure (A) is advanced.

**Active principles of bark of *Aegle marmelos*, Correa.** A. Mookerjee (*Current Sci.*, 1943, 12, 209).—Young bark of both Bengal and Bihar origin yields (a) a coumarin (0.03%), m.p. 123°, (b) an alkaloid (0.003%), m.p. 175°, and (c) umbelliferone. Old bark of both regions yields umbelliferone and a different coumarin (0.6%), m.p. 187—188°; old Bengal bark yields the same alkaloid as the young bark, but old Bihar bark yields a new alkaloid (0.3%), m.p. 142°.

P. G. M.

## VIII.—ORGANO-METALLIC COMPOUNDS.

**Mercurated aliphatic nitriles.**—See B., 1943, III, 280.

## IX.—PROTEINS.

**Chemistry of chromatin.** A. E. Mirsky and A. W. Pollister (*Trans. New York Acad. Sci.*, 1943, [II], 5, 190—198).—A lecture summary of some of the authors' work in this field.

H. W.

(A) **Recovery of crystalline thyroxine from iodinated casein.** (B) **Recovery of *l*-thyroxine by direct acid hydrolysis of iodinated casein.** E. P. Reineke and C. W. Turner (*J. Biol. Chem.*, 1943, 149, 555—561, 563—570).—(A) Iodinated casein (I) is hydrolysed by boiling aq. Ba(OH)<sub>2</sub>, and in 2 experiments 100 g. gave 424 and 385 mg. of cryst. thyroxine (II), m.p. 230—232° (identified by I content, spectrographic absorption, and biological assay), respectively. (I) shows thyroidal activity equiv. to 3% that of *dl*-thyroxine (III). Since (II) is apparently formed in the protein in only the active *l*-form, the highest yield accounts for 28% of the activity of the original protein. Hydrolysis also gives an impure substance (3.4 mg.), insol. in acids, with activity equiv. to 2% of (II). Thus if all activity of (I) is assumed to be due to (II), the thyroidal activity of (I) as measured by the guinea-pig assay, is completely accounted for. (B) Hydrolysis of (I) by equal parts of 32% aq. H<sub>2</sub>SO<sub>4</sub> and BuOH allows the products to be extracted in the BuOH; 0.1% of cryst. *l*-thyroxine (IV), m.p. 236—238°, [α]<sub>D</sub> -4.2° in EtOH-aq. NaOH. 65% I, is isolated. The use of 20% HCl in the hydrolysis gives a lower yield of (IV). (IV) has apparently twice the potency of (III), as shown by its elevation of CO<sub>2</sub> output and loss of body wt. of guinea-pigs. Synthesis of (III) in an iodinated protein is probably due to oxidative coupling of 2 mols. of di-iodotyrosine and the elimination of one side-chain.

A. T. P.

## X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

**Lignin. XLII. Pressure hydrogenation of lignin and lignin-containing waste liquors of the pine.** K. Freudenberg, W. Lautsch, G. Piazzolo, and A. Scheffer (*Ber.*, 1941, 74, [B], 171—183).—Pine lignin (I) is hydrogenated in presence of aq. alkali at 80—140 atm. and ~250° or ~340° in attempts to crack the phenylpropane units with production of *C*<sub>6</sub>H<sub>6</sub>, PhMe, or PhEt derivatives or their hydrogenation products; at ~340° S-containing substances (waste liquors) can be successfully reduced. Using 5% alkali at 260° with a catalyst

of moderate activity, (I) gives 45—50% of phenols, of which 15% [calc. on (I)] are monocyclic [*o*-OH·*C*<sub>6</sub>H<sub>4</sub>·OMe, creosol, *o*-*C*<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, etc.] and traces of nuclear-hydrogenated lignin degradation products. Under the same conditions with Raney Ni or Rupe Ni, 36—40% of nuclear-hydrogenated products are obtained of which 15% consists of cyclohexanols. At 340°, there are formed 13—15% of phenols and (mainly) nuclear-reduced products containing considerable amounts of cyclopentanols; 40% of neutral products, comprising 20% of monocyclic alcohols out of 27% of distillable material, is obtained, thus accounting for 53—55% of (I); the degree of activity of the catalyst or even its presence is of secondary importance. Lignin derivatives containing S (sulphite waste- or black-liquor) are best hydrogenated at 340° without a catalyst, affording corresponding yields of the same products. When *o*-OH·*C*<sub>6</sub>H<sub>4</sub>·OMe, 1:4:3-*C*<sub>6</sub>H<sub>3</sub>Me(OH)·OMe or 1:4:3-CHMe·CH·*C*<sub>6</sub>H<sub>3</sub>(OH)·OMe is hydrogenated at 260°/100 atm. cyclohexanol, 1-methyl- and 1-propyl-cyclohexanol are obtained respectively.

J. WA.

**Lignin. XLIII. Distillation of lignin in hydrogen.** K. Freudenberg and K. Adam (*Ber.*, 1941, 74, [B], 387—397).—The yield of products obtained by dry distillation of lignin (I) is increased in H<sub>2</sub> but only decisively in presence of a hydrogenation catalyst. Ni is used either by pptg. Ni(OH)<sub>2</sub> or NiCO<sub>3</sub> on the (I) or, more simply and better, by passing Ni(CO)<sub>4</sub> over dry (I) at 180°. The Ni-(I) mixture is then heated rapidly to ~220° and temp. increased at such a rate (control necessary at 240°, 320°, and 350°) that distillation is uniform. Small amounts (27 g.) of (I) are distilled in glass tubes; larger quantities (250 g.) in a specially constructed apparatus (illustrated). The Et<sub>2</sub>O-sol. distillates (A) from various (I) generally contained 65—70% of distillable phenols (B). The yields of (A) were larger and those of (B) smaller in the small-scale experiments; the composition of (B) also varied in the two cases. (A) contained small amounts of acids (HCO<sub>2</sub>H, AcOH, and traces of EtCO<sub>2</sub>H) and neutral products [up to 7% of (I)] in addition to (B) [up to 35% of (I)]. The following are identified in the distillate from pine-(I): PhOH, *p*-*C*<sub>6</sub>H<sub>4</sub>Et·OH, guaiacol, *p*-creosol, *o*- and *p*-ethylguaiacol, isoeugenol, *o*-*C*<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, 4:1:2-*C*<sub>6</sub>H<sub>3</sub>Pr(OH)<sub>2</sub> and -*C*<sub>6</sub>H<sub>3</sub>Me(OH)<sub>2</sub>, PhMe, *o*-*C*<sub>6</sub>H<sub>4</sub>Et·OMe, 4:1:2-*C*<sub>6</sub>H<sub>3</sub>Me(OMe)<sub>2</sub>, 2-methylcyclopentanol, cyclohexanediol, MeOH, and EtOH. All the products are in harmony with the view that (I) is a phenylpropane derivative. The residue from the experiments with pptd. Ni(OH)<sub>2</sub> or NiCO<sub>3</sub> ignites in air at 30—40° and can be used as a hydrogenating catalyst.

H. B.

**Lignin. XIII. Cleavage of wood by nitration.** H. Fries and W. Lüdecke (*Ber.*, 1941, 74, [B], 308—313).—Under suitable conditions, e.g., in AcOH or CCl<sub>4</sub>-AcOH, wood meal can be nitrated so that only nitro-N and no ester-N is introduced, no evolution of N oxides is observed, and OMe falls by ~1.7%. The nitro-wood (I) retains its structure and whereas wood cannot be titrated with NaOH (phenolphthalein), (I) consumes 1 mol. of NaOH per NO<sub>2</sub>; this titration is a time reaction and the nitrogenous component dissolves, leaving a swollen cellulosic mass. (I) takes up Na from NaOMe-MeOH without dissolving but H<sub>2</sub>O dissolves out about half of the product, leaving N-free cellulose. Alkali and CS<sub>2</sub> rapidly dissolve (I). No so-called lignin estimation can be carried out with 66% H<sub>2</sub>SO<sub>4</sub>. Wood meal is unaffected by AcOH-NaNO<sub>2</sub>. Isolated lignin cannot be nitrated without partial decomp. or without evolution of N oxides and a sharp fall in OMe (15 → 4%) is observed. Nitrolignin (II) from (I) has 2 N : 27 C whereas ligninsulphonic acid has only 1 S : 27 C, and the latter can be further nitrated. When (I) is treated with Ca(HSO<sub>3</sub>)<sub>2</sub> the (II) is extensively broken down and no insight into the reaction is gained. Methylated wood (OMe 36%) swells on nitration and the product has 1.8% N and 19.3% OMe.

J. WA.

**Beech bark (*Fagus sylvatica*).** I. E. Clotofski, H. Weikert, and H. Nick (*Ber.*, 1941, 74, [B], 299—307).—Distillation of finely-ground bark with superheated steam or steam under reduced pressure gave no identifiable Et<sub>2</sub>O-sol. material. Extraction with org. solvents gives the following recoveries calc. on air-dried bark: EtOH 9.2, COMe<sub>2</sub> 7.6, dioxan 12.8, MeOH 12.2%; other solvents immiscible with H<sub>2</sub>O give poorer results. The hot MeOH extract deposits a fraction (A) on cooling and the material in the mother-liquors is recovered and separated into H<sub>2</sub>O-sol. (B) and H<sub>2</sub>O-insol. (C) fractions. (A) consists of a paraffin, m.p. 63—65°, and a wax giving, on saponification, an alcohol, C<sub>20</sub>H<sub>42</sub>O (arachidyl? or eicosyl?) m.p. 73°, and an acid, C<sub>20</sub>H<sub>42</sub>O<sub>2</sub>, m.p. 57—58°. (B) contains tannins and, on hydrolysis, gives 40% of sugars and 57% of phlobaphens. (C) is separated into Na<sub>2</sub>CO<sub>3</sub>-sol. material, consisting of a mixture of higher fatty and resin acids, and Na<sub>2</sub>CO<sub>3</sub>-insol. material, which, on saponification, gives an alcohol (arachidyl?), m.p. 72.5—73°, Hess' phytosterol, m.p. 132°, a substance, m.p. 225—227°, giving cholesterol reactions, and an acid, C<sub>24</sub>H<sub>28</sub>O<sub>2</sub> (carnaubic?), m.p. 70—71°. The extracted bark (OMe 6.13%) is hydrolysed with 12% H<sub>2</sub>SO<sub>4</sub> (residue 90.9%, OMe 6.78%), then with 65% H<sub>2</sub>SO<sub>4</sub> (residue 42.2%, OMe 12.32%); pentoses, but not hexoses, are liberated in the first stage, and both in the second (phenylosazone, C<sub>18</sub>H<sub>22</sub>O<sub>4</sub>N<sub>4</sub>, m.p. 204—205°). The behaviour of the extracted bark towards Schweitzer's reagent and Na<sub>2</sub>SO<sub>3</sub> is reported.

J. WA.

**Pigment, C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>N, from *Actinomyces*.**—See A., 1943, III, 845.

## XI.—ANALYSIS.

**Purification of substances by partial fusion and warm absorption.**—See A., 1943, I, 320.

**Determination of small concentrations of electrolytes.**—See A., 1943, I, 313.

**Spectroscopic method for the analysis of multi-component mixtures and its infra-red application.**—See A., 1943, I, 319.

**Silver vanadate : use in micro-combustion of organic compounds.** G. Ingram (*J.S.C.I.*, 1943, 62, 175—176).— $\text{Ag}_3\text{VO}_4$  is a satisfactory oxidation filling, which also absorbs halogen and S etc. in the combustion of org. compounds. Possible substitutes for  $\text{PbO}_2$ , prepared by suspending suitable oxides on  $\text{AgCrO}_4$ , are capable of absorbing N oxides.

**Micro-method for halogen determination in organic molecules according to A. Stepanow's principle.** I. Irimescu and E. Chirnoagă (*Z. anal. Chem.*, 1942, 125, 32—37).—The org. substance is dissolved in anhyd. EtOH and metallic Na added. Reaction to form Na halide is soon completed;  $\text{H}_2\text{O}$  is added, and the solution warmed. The halide is then determined gravimetrically as the Ag salt, or by Volhard's method. Reaction is effected in a specially-designed vessel to which a cooling condenser is attached. The method is unsuitable for liquid org. substances. A determination requires 40—70 min. Details of apparatus and procedure, and test data on aromatic org. substances, are recorded. L. S. T.

**Dumas nitrogen determinations.**—See A., 1943, I, 310, 321.

**Micro-analysis of sulphur in organic substances.** N. E. Gelman (*Zavod. Lab.*, 1939, 8, 673—677).—Ter Meulen's semi-micro-method (A., 1934, 424) is adapted to determination of S in 3—5 mg. of volatile or non-volatile org. substances; halogen, As, N, or CNS' does not interfere. The error  $\pm 0.16\%$ . R. T.

**Determination of small quantities of boric acid in organic substances.** E. G. Beckett and M. F. H. Webster (*Analyst*, 1943, 68, 306).—When the sample is ashed with  $\text{Na}_2\text{CO}_3$ , dissolved in conc.  $\text{H}_2\text{SO}_4$ , and heated at  $150^\circ$  with 4:4'-diamino-1:1'-dianthraquinonylamine the optical density at  $\sim 6200 \text{ \AA}$ . is a measure of  $\text{B}_2\text{O}_3$  content. L. A. D.

**Polarographic determination of vanadium [in organic compounds].**—See A., 1943, I, 317.

**Characteristic reactions of citric and tartaric acid.** A. Steigmann (*J.S.C.I.*, 1943, 62, 176).—The hydroxy-pyrroles and -pyridines formed by melting aliphatic OH-acids with  $\text{CO}(\text{NH}_2)_2$  at  $160\text{--}200^\circ$  condense with suitable aldehydes in AcOH solution forming dyes which are characteristic for citric and tartaric acid.

**Effect of citrate on rotation of molybdate complexes of malate, citramalate, and isocitrate.**—See A., 1943, II, 350.

**Anomalous amino-nitrogen values.** H. E. Carter and S. R. Dickman (*J. Biol. Chem.*, 1943, 149, 571—572).—*o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{OH})_2$  submitted to the Van Slyke procedure at  $24\text{--}28^\circ$  for 30 min. give respectively vals. of 0.58, 1.03, and 0.36 atoms of  $\text{NH}_2\text{-N}$  per mol. Similarly, chrysogenin (N-free) appears to contain 2.73% N. Crude penicillin liberates  $\text{N}_2$  from  $\text{HNO}_2$ , although other evidence indicates the absence of  $\text{NH}_2\text{-N}$ . R. L. E.

**Volumetric determination of glucose.** M. Niculescu and N. Căplescu (*Z. anal. Chem.*, 1943, 25, 416—423).—The glucose (I) solution is oxidised by warming with standard aq.  $\text{K}_2\text{Cr}_2\text{O}_7$  and conc.  $\text{H}_2\text{SO}_4$ . After dilution, the excess of  $\text{K}_2\text{Cr}_2\text{O}_7$  is found by titration with aq.  $\text{Fe NH}_4$  sulphate solution, using  $\text{K}_3\text{Fe}(\text{CN})_6$  as external indicator. The (I) to be determined should be 10—25 mg. and the quantities of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$  given must be adhered to. Test data and details of procedure are given. L. S. T.

**Determination of free and bound hexuronic acid.** K. Freudenberg, H. Gudjons, and G. Dumpert (*Ber.*, 1941, 74, [B], 245—247).—Apparatus and technique are described for decomp. hexuronic acids and polyuronides in a stream of  $\text{N}_2$  with 20M- $\text{ZnCl}_2$  solution at  $160\text{--}165^\circ$  and collecting  $\text{CO}_2$  after suitable removal of furfuraldehyde and other anticipated volatile products. J. WA.

**Determination of amino-acids by the solubility-product method.** S. Moore and W. H. Stein (*J. Biol. Chem.*, 1943, 150, 113—130).—The principle of the method is that the solubility at  $0^\circ$  of a sparingly sol. salt of an  $\text{NH}_2$ -acid [that formed with an aromatic sulphonic acid (I) is normally used] is determined in the solution under investigation with and without the addition of a known amount of free (I). From the results and the (previously determined) solubility product of the salt, the concn. of the  $\text{NH}_2$ -acid in the solution is calc. The theory of the method as applied to the determination of leucine (II) and glycine (III) is discussed, and the experimental technique is described in very full detail. 1:2:5- $\text{C}_6\text{H}_3\text{MeBrSO}_3\text{H}$  is suitable for (II), and 5:1- $\text{NO}_2\text{-C}_{10}\text{H}_6\text{SO}_3\text{H}$  for (III). Other  $\text{NH}_2$ -acids interfere only in certain unusual circumstances. Using this method, the (II) content of ovalbumin was found to be 9.0%, and the (III) content of silk fibroin 43.8%. E. C. W.

**Use of glass fluorescent standard in the determination of aneurin (vitamin- $B_1$ ).** G. Vastagh and F. Szeghő (*Z. anal. Chem.*, 1942, 125, 23—32).—The conditions under which the Zeiss glass fluorescence standard can be used in the thiochrome method for determining vitamin- $B_1$  have been investigated. The relationship between the quantity of  $B_1$  and the fluorescence intensity obtained with the glass standard is not linear. This is due, not to optical causes, but mainly to the unfavourable distribution coeff. between the aq. alkaline solution and the  $\text{Bu}^\beta\text{OH}$  solution of thiochrome (I), which makes quant. extraction difficult. Filter-paper and the  $\text{Bu}^\beta\text{OH}$  itself also have a fluorescence that cannot be neglected. Addition of NaCl improves extraction. The procedure described for the oxidation of  $B_1$  to (I), the extraction of (I), and the use of the glass standard permits the employment of a type of step photometry to the determination of  $B_1$  without the repeated prep. of comparison solutions. L. S. T.

**Determination of piperazine.** HI. A. Castiglioni (*Z. anal. Chem.*, 1941, 121, 347—348; cf. A., 1941, II, 388).—10 c.c. of piperazine solution in 95% EtOH are treated with 10 c.c. of 5%  $\text{H}_2\text{C}_2\text{O}_4$  in 95% EtOH, and the whole is set aside for 8—10 hr. The ppt. is collected, washed with 95% EtOH, dried at  $100\text{--}105^\circ$ , and weighed.  $(\text{CH}_2)_6\text{N}_4$  gives a ppt. with  $\text{H}_2\text{C}_2\text{O}_4$ , and must be absent. Salicylic and quininic acids do not interfere. L. S. T.

**Nephelometric determination of nicotine.** K. B. Trifonova (*Zavod. Lab.*, 1939, 8, 731).—Nicotine is determined by comparing the turbidity developed in test and standard solutions on addition of 1% silicotungstic acid. R. T.

**Detection of native protein with pH indicators.** M. Ishidate and T. Sakaguchi (*Ber.*, 1941, 74, [B], 163—170).—The protein error (P.E.) of indicators is further developed as a spot test for native protein (cf. Feigl and Anger, *Mikrochim. Acta*, 1937, 2, 107). Of 27 indicators used, tetrabromophenolphthalein ester (I) is the most sensitive as it can detect casein, haemoglobin, ovalbumin, and gelatin in limiting concns. of 0.004—0.005% (2—2.5  $\mu\text{g}$ .); next in order come Congo-red, bromophenol-blue, dimethyl-yellow, and metanil-yellow. Only dyes effective as pH indicators in the range 1.2—5.5 are found to be effective, and the P.E. is max. at about the isoelectric point and min. at pH  $\sim 2.5$ . The P.E. is first determined and then the protein is broken down with HCl or NaOH and, after neutralisation, the P.E. is again determined. Differences are marked with (I) and negligible with other indicators. J. WA.

**Determination of gelatin.**—See A., 1943, III, 928.

**Total nitrogen content of ovalbumin and other proteins.** A. C. Chibnall, M. W. Rees, and E. F. Williams (*Biochem. J.*, 1943, 37, 354—359).—The Kjeldahl process may give low vals. for the N content of proteins. This is due to the digestion period being too short (with proteins and protein hydrolysates it should be continued for  $\leq 8$  hr. after the digest has cleared) and to the pronounced hygroscopic activity of anhyd. proteins which necessitates that moisture and N contents should be determined on separate samples of air-dried material. Using the technique described, the following vals. have been obtained for the N content of moisture- and ash-free protein: ovalbumin (native and uncoagulated) 15.76, edestin 18.7,  $\beta$ -lactoglobulin 15.58, casein 15.73, amandin 18.75, insulin 15.54, and horse carboxyhaemoglobin (moisture- but not ash-free) 16.8%. H. G. R.

**Foreman method for determination of dicarboxylic acids in protein hydrolysates.** K. Bailey, A. C. Chibnall, M. W. Rees, and E. F. Williams (*Biochem. J.*, 1943, 37, 360—372).—Cystine (I) in the hydrolysate undergoes partial dismutation into the sulphinic and sulphonic acids during treatment with CaO and is pptd. with the Ca dicarboxylates by EtOH together with small amounts of (I), tyrosine, serine (II), and other bases. The Ca salts of the dismutation products are very insol. and interfere with the determination of aspartic acid (III) as Ca salt (IV). (I) may be removed as the  $\text{Cu}^I$  mercaptide prior to the CaO-EtOH treatment. A small amount of the more insol.  $\text{NH}_2$ -acids (methionine, tyrosine, leucine, and phenylalanine) contaminates the mercaptide ppt. but there is no loss of dicarboxylic acids or arginine and the purity of (IV) is such that no crystallisation is necessary. Significant amounts of both (III) and glutamic acid (V) may be isolated from the CaO-EtOH filtrate after removal of the bases and most of the  $\text{NH}_2$ -acid. The solubility of the Ca glutamate is relatively high, especially when some of the acid is *dl*-, but that of (IV) appeared to be small. A modified procedure gives vals. for the (III) and (V) contents of proteins accurate to within 2%. The application of solubility correction to results obtained by one complete CaO-EtOH treatment gives vals.  $>$  those in literature. The "hydroxyglutamic acid" fractions previously reported are mixtures of (III) and (V), dibasic dismutation products of (I), and (II) and its decomp. products in varying proportions, and no indication of the presence of any other dicarboxylic acid has been obtained. The results obtained by previous workers with Foreman's method are valueless from the point of view of the Bergmann-Niemann hypothesis. H. G. R.